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EVALUATION OF SWELLING PROPERTIES OF POLY (ACRYLIC ACID)/Zr-PILLARED K10 SUPERABSORBENT HYDROGEL[*]

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ABSTRACT

Zr- Pillared K10 (Zr-K10) was synthesized by using Montmorillonite K10 clay. Zr- pillared K10 based superabsorbent (Zr-PILC-SA) was synthesized by using Zr- pillared- montmorillonite K10 via graft copolymerization reaction of acrylic acid (AA). After preparation of the films of hydrogels of Zr- pillared K10, swelling studies were performed in distilled water and different pH values at room temperature to investigate swelling behavior of pillared clay based superabsorbent films. It was also obtained that Zr-K10 based superabsorbent was pH dependent and showed a reversible swelling behavior. The swelling behavior of Zr-K10-SA was increasing by decreasing amount of Zr-K10 in the hydrogel. SEM, FTIR and XRD analysis were conducted for further characterization of the Zr-PILC-SA. FTIR analyses lead to ester formation between Zr-K10 and SA. XRD revealed the morphology of the superabsorbent was exfoliated and the layers of clay dispersed on the composite.

1. INTRODUCTION

Superabsorbents are capable of absorbing and retaining huge amounts of aqueous fluids even under some pressure (Wang et al., 2008). Superabsorbent polymers are used mainly as absorbents in healthcare and agriculture applications and are commonly based on acrylic monomers such as acrylamide, acrylic acid (AA) (Li et al., 2004). However, most of the superabsorbents used as disposable materials are expensive synthetic polymers (Li et al., 2004, Lin et al., 2001), their production consumes a lot of petroleum resource and their usage can also cause a non-negligible environment problem (Wu et al., 2000). Thus the utilization of low-cost resources for preparing superabsorbent and the design and synthesis of multicomponent superabsorbent based on natural materials have been subjects of great interest (Zhang et al., 2006, Weaver et al., 1976). Adding inorganic materials was caused decrease cost amount in production of superabsorbent hydrogels. Pillared clay was used as additive material in the synthesis to decrease production cost of hydrogels in this study.

Pillared clays are layered materials prepared by the exchange of compensating cations for oligomeric or polymeric hydroxymetals, followed by calcination. The calcination promotes the dehydration and dehydroxylation of the polycations, with the formation of metal

[*] The first version of this paper is presented in the "2nd International Rating Academy Congress: Hope" held in Kepez / Çanakkale on April 19-21, 2018.

oxides that act as pillars, maintaining the separation between the layers with the appearance of interlayer and interpillar spaces with molecular dimensions (Figueras, 1988, Vaughan, 1988, Gil, et al., 2000, Cheng, Yang, 1997). The first step in the pillaring process is to prepare a pillaring agent. Zr-pillared clays (Zr-PILCs) were prepared from zirconyl chloride solutions. For synthesis of pillared clay catalysts, Montmorillonite K10 (K10) was used as precursor material. In this study, zirconium pillared montmorillonite K10 samples were prepared for synthesis poly (acrylic acid)/Zr-pillared clay superabsorbent composites. Using Zr-pillared K10 as additive of superabsorbents is the new approach. The preparation of superabsorbent composites is beneficial owing to develop mechanical and materials properties because of negative features such as high production cost and low gel strength. Additionally, clays have been more suitable for use in water absorbents as additives because of their hydrophilic nature. The swelling behavior of polymer/clay superabsorbent composites in water were studied and organic solvents has rarely been discussed.

The present study deals with the synthesis and characterization of Zr-K10 and Zr-PILC containing acrylic based superabsorbent hydrogel composites. The effect of pH values on the water absorbency of the superabsorbent composites containing Zr-K10 was investigated. Moreover the performance of inorganic filler amount on the properties of the superabsorbents was compared each other in detail. Additionally, the characterization of pillared clays containing acrylic-based superabsorbent hydrogel composites was carried out by XRD, FT-IR, and SEM.

2. MATERIAL AND METHODS

2.1.Reagents and Materials

Acrylic acid (AA) monomer and the crosslinker N, N′-methylene–bisacrylamide (MBA) purchased from Fluka were used without further purification. Ammonium persulfate (APS), sodium metabisulfite (SMBS) and potassium hydroxide (KOH) (all from Merck) were used as received.

Montmorillonite K10 (K10) used in this study was supplied from Fluka Company (Cat. No. 69867) was utilized as precursor material of Zr-PILC. Chemical composition of Montmorillonite K10 is 69.0% SiO2, 14.0% Al2O3, 4.5 0% Fe2O3, 2.0 % MgO, %1.5 CaO, <0.5% Na2O, 1.5% K2O, and 7.0% loss on ignition. K10 has a surface area of 197 m2/g and cation exchange capacity of K10 is 30 meq/ 100g. BET surface area (SBET) of Zr- K10 was obtained from N2 adsorption– desorption isotherms at 77 K, measured on SORPTOMATIC 1990 after a degassing under vacuum for 3 h at 150 ºC by using MILES-200 Advanced Data Processing Sorption Software Version 3.00. Zr- K10 has a surface area of 237.08 m2/g.

2.2. Synthesis of Zirconium Pillared Montmorillonite K10 (Zr-K10)

Zr-K10 was prepared from zirconyl chloride solution. In a first set of preparation, 0.2 M $ZrOCl_2.8\ H_2O$ solution was previously refluxed at 95 °C for 5 and 24 h. The solution re-fluxed for 5 h remained limpid, but it turned turbid after refluxing for 24 h. The solutions were added dropwise to 2 wt% (%50 acetone %50 H_2O) suspension of K10 at a rate of 10 mequiv. Zr g^{-1} clay. The final suspensions were stirred for 24 h at room temperature. Samples were further aged for 10 days. The pillared clays were washed by dialysis and oven-dried. After this period, the samples were calcined at 250 °C for 2 h.

2.3. Preparation of the Superabsorbent Composite

The poly (acrylic acid)/Zr-pillared clay superabsorbent composites were synthesized through the graft copolymerization of acrylic acid on pillared clay with MBA as a crosslinker and APS as an initiator in an aqueous solution. The inorganic pillared clay particles in the

network acted as additional network points (Li et al., 2004). Acrylic acid (20 g) was neutralized with potassium hydroxide solution (12.1 g KOH +10.0 g H_2O). After the neutralization, MBA solution (0.013 g MBA + 3.0 g H_2O) was added to the monomer solution. The mixture was poured into a 600-mL beaker, which was equipped with a magnetic stirrer and thermometer. 0.05, 0.10 and 0.20g of Zr-K10 were added to monomer solutions and stirring was continued until homogeny mixtures were obtained. To start polymerization reaction, the APS solution (0.05 g APS +1.5 g H_2O) and the SMBS solution (0.063 g SMBS + 2g H_2O) were added to the mixture. The temperature of mixture was increase rapidly to almost 100°C within a few minutes. Prior to hardening the products, the mixtures were pour into the Petri dish to obtain thin films. Samples were dried in a vacuum oven at 70°C for 24 h and then a few amount of water was dropped to film and after 1 h, the film was removed from Petri dish and dried again.

2.4. Measurement of Water Absorbency

Water absorbency measurement was performed weighing dry sample (m_0) and water-swollen sample at time t (m_t) at room temperature, respectively. The percent of swelling values were determined from the following equation (El Hamshary, 2007).

$$\%Swelling = 100\left[\frac{(m_t - m_0)}{m_0}\right] \quad (1)$$

The swelling measurements were made thrice and the average data was used for calculations.

2.5. Measurement of the Swelling Rate

Dry film superabsorbents composite samples were firstly weighed and then immersed in 20 mL of distilled water at room temperature. The weighing swelling ratios of samples were performed at various times. The swelling ratios of superabsorbents were calculated by equation (1). Swelling equilibrium times were determined via this process.

2.6. Characterization of Pillared Clays and Zr-K10 Based Superabsorbents

Fourier transform infrared (FTIR) spectra were recorded on a FTIR Perkin Elmer Spectrum BX-II in the 4000–400 cm-1 region using KBr pellets for pillared clays and ATR probe for superabsobent films. Morphology of the samples was examined using a Jeol JSM 60 SEM operating at the accelerating voltage of 20 kV after coating the sample with a gold film. X-ray powder diffraction patterns were obtained by Rigaku Dmax 2200/ PC model instrument with Cu K radiation (40 kV, 40 mA). XRD measurements of superabsorbents were performed by film form. For clays and pillared clays, analysis was process to powder form. The change of clay layer space by pillaring and preparing superabsorbents was found out by means of Bragg equation ($2d\sin\theta = n\lambda$). XRD reveals the basal spacing of the pillared clays before and after in-situ incorporation indicating the morphology of the superabsorbent (exfoliated, intercalated or only dispersed).

3. RESULTS AND DISCUSSION

3.1. Swelling Rate Measurements

Figure 1 displays the swelling rate of Zr-K10 based superabsorbents. It was found that the swelling ratio of superabsorbent hydrogel containing 0.05g of Zr-K10 was higher than superbsorbents containing 0.10 and 0.20g of Zr-K10 at swelling equilibrium, respectively.

Additionally, the swelling rate of Zr-K10 (0.05g)-SA was the highest than the others and the time needing to reach swell equilibrium increases with increase of pillared clay amount. Zr-K10 based superabsorbents reached equilibrium at about 120 min. The percentages of equilibrium swelling values were at about 12500 for Zr-K10 (0.05g)-SA, at

about 11500 for Zr-K10 (0.10g)-SA and at about 10850 for Zr-K10 (0.20g)-SA. This may be attributed to crosslink density and elasticity of polymer network. Pillared clay act as crosslinking points because of carrying –OH groups in their structure. The carboxylate groups of the polyacrylate chains may react with -OH groups of pillared clays. Increasing the amount of pillared clays in the polymeric network resulted in the generation of more crosslink points that increase the crosslink density of the composite, and then the elasticity of the polymer chains decrease. It was deduced that more crosslink points may occur between Zr-K10 (0.20g) pillared clay and SA. Shortly, the superabsorbent with lower pillared clay content had a higher initial swelling rate and higher water absorbency and required less time to reach swelling equilibrium.

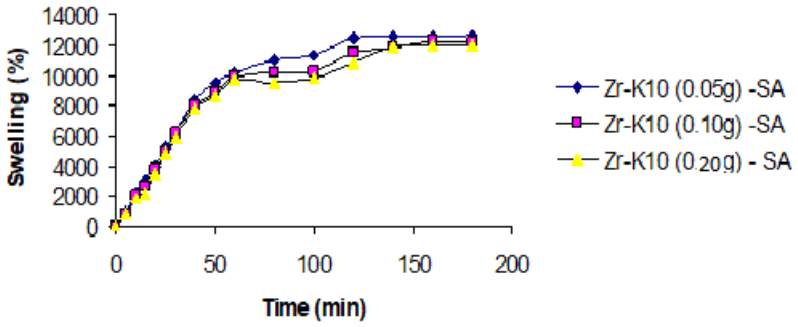

Figure 1. Swelling kinetics of superabsorbents composite in distilled water

3.2. pH-Sensitivity of the Superabsorbents

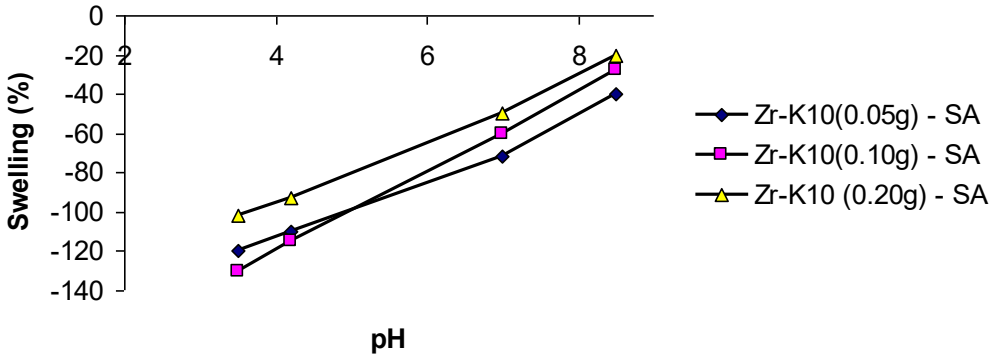

Figure 2. Effect of pH on the equilibrium swelling of superabsorbents

To reveal pH sensitivity of pillared clay based superabsorbents, firstly the films were immersed in distilled water and then in different buffer solutions until swelling equilibrium. Figure 2 showed the effect of the pH on water absorbency of superabsorbents. The buffer solutions at pH 3.5, 4.2, 7.0 and 8.5 were prepared by using citric acid and $Na_2HPO_4.2H_2O$ solutions. The absorbency of the superabsorbent composite increased sharply as the pH increased from 3.5 to 8.5. The superabsorbent composites were sensitive to the pH change. Shrinkage was occurred at acidic pH for all Zr-K10 based superabsorbents. The change in the swelling ratio by changing pH may be explained by Lee and Wum suggestion (Lee, Wum, 1996); in an acidic environment, the $–COO^-$ groups on the polymeric chains turn into –COOH groups, while the –COOH groups on the polymeric chain turn into $–COO^-$ groups in basic

solutions, and this behavior was interpreted as a buffer action of –COOH and –COO⁻. In the acidic environment, the repulsion between polymeric chains decreases, which leads to the decrease of water absorbency. The –COOH groups present within the network remain almost nonionized, thus imparting almost non-polyelectrolyte type behavior to the hydrogel (El-Hamsary, 2007). Furthermore, there exist H-bonding interactions between carboxylic groups of acrylic acid and amide groups of acrylamide. These H-bonding interactions result in the formation of a compact or tight structure which does not permit much movement of polymeric chains within the hydrogel network, which lead to minimum swelling of hydrogel (El-Hamsary, 2007). The ionization of the carboxylic acid groups of the gel occurred. More hydrophilic polymer was occurred at higher pH value because of ionization of the carboxylic acid group and contributed to the higher water absorption. As seen in Figure 2, the swelling behavior of Zr-K10 based superabsorbent films seem to be pH dependent. The content of pillared clay in the network of the superabsorbent affected the swelling ratio. More shrinkage and lower swelling was obtained by increasing the content of Zr-K10 in the polymeric network. Additionally, crosslinking might be increased in order of increasing the amount of pillared clay. The water content decreased due to increased level of crosslinking (Wu et al., 2003).

3.3. Swelling Reversibility of Superabsorbents

To clarify swelling reversibility, the Zr-K10 based superabsorbents were equilibrated at pH=1.2, and then alternated between solutions at pH=7.4 and pH=1.2 for about 120 minutes, respectively. A swelling was measured at about 910% for Zr-K10 (0.05g)-SA, 290% for Zr-K10 (0.10g)-SA and 230% for Zr-K10 (0.20g)-SA at pH= 7.4, respectively. Then the films put into pH=1.2 for 120 min. and approximately 12.0%, 42.0% and 142.0% deswellings for Zr-K10(0.05g)-SA, Zr-K10(0.10g)-SA and Zr-K10(0.20g)-SA, respectively were determined. Besides, when the superabsorbent films altered from acidic to basic buffer and then to acidic buffer, pillared clay based superabsorbents showed a reversible swelling behavior with relatively fast response. Zr-K10 (0.05g)-SA had the fastest response to pH change. It can be added that reversible swell-shrink properties of pillared clay based superabsorbents would be beneficial characteristics for pH sensitive systems with controllable swelling ability. Also, this result indicates that the PAMA composite can be used as a recyclable water-managing material for the renewal of arid and desert environment (Zhang et al., 2006).

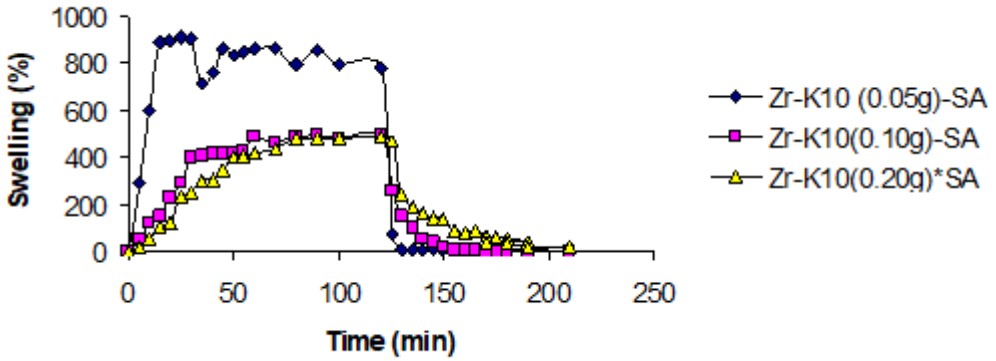

Figure 3. pH-dependent reversible swelling behavior of superabsorbents (Superabsorbents equilibrated at pH=1.2, then alternated between solutions at pH=7.4 and pH=1.2)
Concentration set design for the preparation of PCR and PLS calibrations

3.4 SEM Images

The SEM micrographs of Zr-K10, Zr-K10 (0.05g)-SA, Zr-K10 (0.10g)-SA and Zr-K10 (0.20 g)-SA were exhibited in Figure 4. A considerable difference was observed between pillared clay and superabsorbents. Polymeric network was predominant in superabsorbent hydrogel morphology. When the content of pillared clay was increased, the surface of polymeric network was affected, the signs of pillared clay were increased and surface of hydrogels were less smooth. Also SEM micrographs were supported the homogeneity of composed superabsorbents after graft polymerization had been occurred. Homogenous dispersion of pillared clay particles may be contributed to more crosslinking structure. Furthermore more crosslinking might be obtained by increasing pillared clay amount in the superabsorbents. SEM micrographs of superabsorbents clearly represented lower swelling capacities because of their highly rigid type structure.

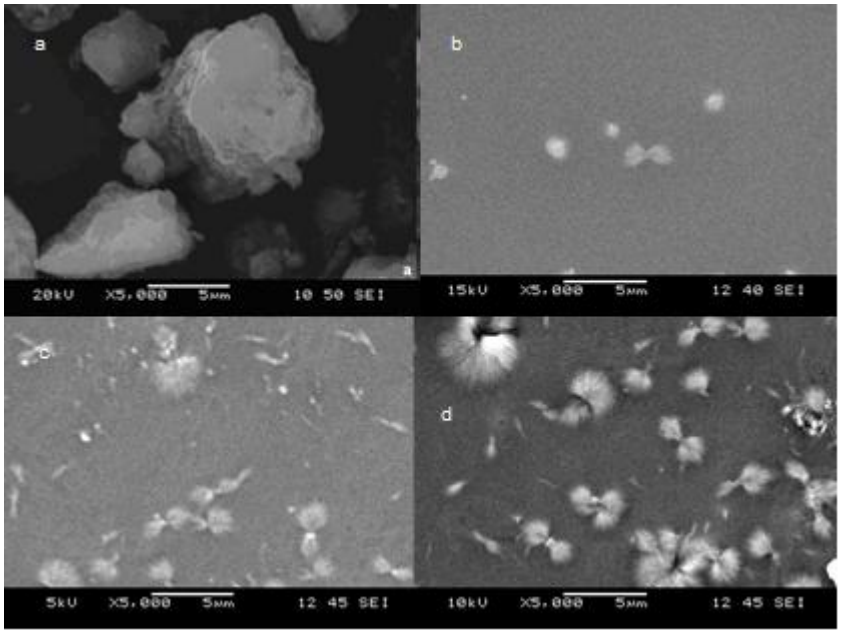

Figure 4. SEM micrographs of (a)Zr-K10 (b)Zr-K10(0.05g)-SA (c)Zr-K10(0.10g)-SA (d) Zr-K10(0.20g)-SA (5000x magnification).

3.5. FT-IR Analysis

Clays - pillared clays and superabsorbents were analysed by using KBr disks and ATR prope, respectively. Consequently the characteristic FTIR bands of clays and superabsorbent composites were summarized in Table 1.

Table 1. The characteristic FT-IR data of the samples

IR bands	Samples				
	K10	**Zr-K10**	**Zr-K10(0.05g)-SA**	**Zr-K10(0.10g)-SA**	**Zr-K10(0.20g)-SA**
Al_2OH(octahedral layer) (cm^{-1})	3654	3650	3645	3642	3652
Stretching vibrations of H_2O(cm^{-1})	3410	3420	3398	3450	3420
Stretching vibration of $–CH_2$ (cm^{-1})			2980-2870	2970-2862	2982-2871
Stretching vibration of C=O (cm^{-1})			1732	1725	1745
Bending vibrations of H_2O(cm^{-1})	1636	1630	1678	1685	1638
Asymmetric vibration of R-COOK (cm^{-1})			1554	1550	1538
Bending vibration of $–CH_2$(cm^{-1})			1457	1450	1445
Symmetric vibration of R-COOK (cm^{-1})			1412	1405	1402
Asymmetric stretching vibrations of SiO_2 tetrahedra(cm^{-1})	1045	1040	1075	1072	1070
Bending vibrations of Al_2OH(cm^{-1})	917	921	915	917	913
	842	843			
Stretching vibration of Al^{IV} tetrahedra(cm^{-1})	798	800	802	800	805
	673	692			
	615				
	590				
Bending vibration of Si-O(cm^{-1})	524 468	525 469	520 480	524 470	525 465

A broader band around 3620 cm-1 for all samples, in the –OH stretching region are attributed to Al2OH group (3650 cm-1) of the octahedral layer. Stretching vibrations of water molecules may also contribute to –OH peaks (3500 cm-1). On pillaring, the band broadens due to the introduction of more –OH groups of the pillar, which is interpreted as an effect of pillaring. The broad absorption bands observed in K10, Zr-K10 and Zr-K10 containing superabsorbents at 3410, 3420, 3398, 3450 and 3420cm-1, respectively represents the fundamental stretching vibrations of different –OH groups present in Mg–OH–Al, Al–OH–Al and Fe–OH–Al units in the octahedral layer. The shift of these bands is also observed for Zr-K10 based composites. The other explaining for this is that the networks of superabsorbents contain pillared clays and the graft copolymerization between OH groups on clays and monomers take place during the reaction. Bands around 1600 cm-1 are due to bending vibrations of water. The band around 1045 cm-1 is due to asymmetric stretching vibrations of SiO2 tetrahedra. After polymerization, stretching vibrations of SiO2 tetrahedra was shifted to around 1075 cm-1 for Zr-K10 based composites, respectively. It indicates the esterification of carboxylic acid with silanol. This mechanism was supported by shifting of the OH stretching vibration of clays and pillared clays. These results may confirm the grafting

reaction between pillared clays and the acrylic network through ester formation. A band around 800 cm-1 is due to stretching vibration of AlIV tetrahedra, when substitution of Al for Si is low; Al2OH libration lies in the 915±950 cm-1 range, and absorption at 526–469 cm-1 is due to bending of Si–O vibration. These IR characteristic bands of clay were observed and only little shifts of were noticeable in pillared clays and the network of pillared clay based composites from Table1. The little shifts of these all bands showed that the basic clay layer structure remains unaffected on pillaring and polymerization. These results suggested that the pillaring agents physically entrapped within the PILC structure.

The FTIR data gave a distinct absorption band at about 1730 cm−1 for only composites. This band was belong to the C=O stretching vibration. The bands corresponding to the –C–H stretching of acrylate unite was observed around 2980 and 2870 cm-1 for composites. The bands at around 1450 cm-1 were attributing to the bending vibration bands of –CH2 for composites. Asymmetric and symmetric vibrations of R-COOK groups appear at about 1550 and 1040cm-1 for the superabsorbents. Eventually ester formation is occurred by graft polymerization reaction.

3.6. XRD Analysis

The X-ray diffraction patterns of Zr-K10, Zr-K10 (0.05g)-SA, Zr-K10 (0.10g)-SA and Zr-K10 (0.20g)-SA were performed. The lattice spacings of montmorillonite K10 and Zr pillared K10 were summarized in Table 2. 001 lattice spacing of K10 was increasing by pillaring with Zr polyoxications. After polymerization with pillared clays the diffraction peak corresponding to the montmorillonite (d001 basal spacing of montmorillonite layers) was not observed at about 2□=5.0-6.0°. The absence of this peak indicates that the montmorillonite layers are exfoliated or highly expanded. The expansion mechanism probably originates from the growing polymer chains by adsorbed monomers on the clay layers pushing apart the layers even in high clay loadings. Layers of montmorillonite were completely dispersed in a continuous polymer matrix as single layers.

Table 2. XRD results of montmorillonite K10 and Zr-K10

	Samples	
	K10	Zr-K10
2θ	5.94°	5.21°
d_{001} (Å)	14.83	16.93
d_{001}- 9.6 (Å)	-	7.33

4. CONCLUSION

In this present study, swelling characters of composites were revealed out after grafting occurred between pillared clays and the acrylic network. It was found that swelling degree and fast response to pH change of the pillared clay based superabsorbent hydrogels was decreasing by increasing the content of the pillared clay in the network of the hydrogel. The swelling rate of Zr-K10 (0.05g)-SA was higher than Zr-K10 (0.10 g)-SA and Zr-K10 (0.20 g)-SA. Additionally, the time needed to reach swelling equilibrium decreased with decrease of pillared clay content. The swelling values of superabsorbents were significantly increased with the raise of pH in the range 3.5 -8.5.

FTIR analysis and SEM micrographs impressed that the pillared clay based superabsorbents were successfully obtained. Besides, XRD analysis of the samples showed

that layers of montmorillonite were exfoliated in the hydrogel structure and were completely dispersed in a continuous polymer matrix as single layers.

Clays and pillared clays might be added to superabsorbent hydrogel to compose economic products. Modifying of poly (acrylic acid) composites with inorganic materials affected the swelling character and product cost. Decreasing of swelling ratio was observed by increasing the content of pillared clay. All Zr- K10 based poly (acrylic acid) composites were pH sensitive. The behavior of shrinkage at acidic and swelling at basic environment was useful for pH sensitive systems with controllable swelling ability such as controllable drug delivery. Also, the character of water absorbing and swelling reversibility was indicator of suitable applications in agriculture and horticulture.

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STUDENTS' UNDERSTANDING OF GAS CONCEPTS[*]

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ABSTRACT

The main purpose of the present study was to investigate second year classroom teacher education students' misconceptions and learning difficulties related to gas concepts. The study was carried out during the last academic year at a state university in Turkey. About 100 second year students were the participants of the study. Gas Concept Test developed by Yalçınkaya (2010) was administered to the students to determine the students' misconceptions and their understanding of gas concepts. The results revealed that the students had misconceptions, such as gas particles expand when heated, shrink when cooled; particles are unevenly scattered in any enclosed space; particles rise and stay away from heat, etc. The misconceptions and learning difficulties of the classroom teacher students should be remedied by suitable conceptual change strategies. So, these erroneous ideas cannot pass on primary pupils.

1. INTRODUCTION

Misconceptions or misunderstandings are information that have evolved from the personal experience of the individual, are far from science, prevents the teaching of concepts verified scientifically (Yürük, Çakır, & Geban, 2000). In order for a student's knowledge to be counted as a misconception, it is necessary for the idea to have three conditions; the knowledge of the student is not scientifically appropriate, the student tries to search for scientific evidence to defend this false idea, and the student is confident in her/his own answer (Eryılmaz & Sürmeli, 2002).

The source of the misconceptions arising from experiential and instructional reasons (Skelly & Hall, 1993 as cited in Nakiboğlu, 2006, 200) are the preliminary information, spoken language, analogies and metaphors, models and symbols, and textbooks and teachers (Nakiboğlu, 2006, 201-202). The misunderstanding that comes from teacher involves all these factors that lead to the misconception, because the language of the teacher, the textbook the teacher used inadequacy of teacher's subject knowledge and if the teacher ignores the pre-knowledge and misconceptions of their students result with misconception (Nakiboğlu, 2006, 202-203).

Misconceptions are the greatest obstacle in learning. Failure to intervene in these obstacles will lead to erroneous learning. Demir and Sezek (2009) stated that misconceptions

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that were not taken care of were transferred to upper classes, and if the mistakes of teacher candidates could not be resolved, they would be passed on to the students. Dikici, Türker and Özdemir (2010) stated that the factors such as psychology, environment, socio-cultural structure are the obstacles in front of the meaningful learning of the students. These factors indicate that misconceptions can also arise from students. In order for meaningful learning to take place, it is necessary to establish links between newly learned concepts and old concepts. Elimination of misconceptions at elementary level facilitates meaningful learning (Bal & Koray, 2002).

Chemistry is a science that examines the matter and relations between matters. In relation to this discipline, students need to correctly structure the concept of "matter" and especially the properties of solid, liquid and gas in their minds in order to because they constitute a base for other concepts as well (Birinci Konur and Ayas 2010).

Lawrenz, Lin, and Cheng (2000 as cited in Morgil et al, 2003) investigated the misconceptions existed in students and teachers after Boyle, Charles, and ideal gas laws have been processed and found that half of students and teachers made incorrect comments on the problem of volume-temperature, and 80 % of the students gave inadequate and incorrect answers to the solution of conceptual problems. Boyle's law describes the relationship between the pressure and volume of a gas under relatively normal conditions (close to room temperature and pressure). Boyle's law states that, when holding temperature constant, the pressure of a gas is inversely proportional to its volume (Maeng & Randy Bell, 2013). Charles's law is the direct relationship between the temperature and volume of a gas (Maeng & Randy Bell, 2013). Ideal gas law describes the relationship between pressure, volume, moles, and temperature of a gas or PV=nRT (Maeng & Randy Bell, 2013).

One of the concepts of abstract science that students have difficulty in understanding is the concept of gas pressure (Şahin & Çepni, 2012). It has also been revealed in the literature that prospective teachers have difficulty in establishing relations between the concepts that constitute the factors affecting the state of gases such as temperature, volume and pressure in gas, and they have inadequate meaning and some misconceptions (Birinci Konur & Ayas 2010; Nakiboğlu & Özkılıç Arik, 2006).

Although there are studies in the literature about classroom teacher education students' understanding of the particulate nature of the material, such studies are mostly in the level of secondary education. It becomes important to determine what gases mean to candidate teachers who will become classroom teacher when they graduate (Birinci Konur & Ayas, 2010).

Chemistry has three basic components; the macrochemistry of the tangible, edible, visible; the submicrochemistry of the molecular, atomic and kinetic and the representational chemistry of symbols, equations, stoichiometry, and mathematics (Johnstone, 1983 as cited in Johnstone, 1993). The correct understanding between these dimensions makes it easier for students to understand chemistry. The fact that students have great mental gaps between micro- and macro-dimensions makes it difficult for them to correlate macroscopic events with microscopic events and to bridge these gaps (Çavdar, Okumuş, Alyar, & Doymuş, 2016). The fact that the particulate nature of matter is first taught in the primary school (Çavdar et al., 2016) by the classroom teachers, the education of the classroom teacher candidates on these misconceptions becomes important in terms of not moving these errors to future generations**.**

2. MATERIAL AND METHODS

In this study, which is aimed to determine the conceptions of pre-service classroom teachers about gases, a survey model was used. The survey model is a research approach aimed at describing the existing situation (Karasar, 2009, p.77).

The participants were 107 freshmen students attending to classroom teacher education department at Niğde Ömer Halisdemir University in Turkey. Since the sample can be accessed and selected from the group in which the application can be performed, appropriate sampling is used for non-arbitrary sampling methods (Büyüköztürk, 2012).

Based on General Chemistry is the name of the course classroom teacher candidates take for one semester. The course is a theoretic lesson and takes two lesson hours. Properties of matter, elements and compounds, chemical reactions, reaction stoichiometry, states of matter, solid and gas state structure of matter, mineral forms, changes in form of matter; solutes and mixtures, acids and bases, carbon compounds, solubility and precipitation, oxidation and reduction, and chemistry of life are the subjects taught at this course.

The Gas Concept Test developed by Yalçınkaya (2010) was used as a data collection instrument in the study in order to explore first grade classroom teacher candidates' conceptions about gases. This test included 26 multiple choice items with five alternatives. Possible misconceptions were included in the alternatives of the multiple-choice test items. The test forms were administered during one lesson hour to the classroom teacher education students.

Students' responses to the test form were saved in the SPSS data file and frequency analyses for each item were performed. The proportion of incorrect responses given to an alternative was used to determine misconception. This means that when more than 20% of the teacher candidates chose the incorrect alternative, this alternative was considered as a misconception held by these students. If the proportion is less than 20 %, it was not taken as a misconception.

3. RESULTS

1. Which of the following is true about the gases?

Item 1 was about the general properties of gases. As seen from the Table 1, majority of students (69%) was aware that there are almost non-existing forces between gas particles. When Birinci Konur and Ayas (2010) studied the gas molecule drawings of classroom teacher education students in order to determine how the students constructed the gas concept in their minds, they realized that 34% of the students made accurate explanations about gas molecules and drawings supporting these explanations. In the explanations made about these drawings, students used the expression "the distance between molecules is less than that of solid and liquid".

Table 1. Students' Selection of Alternatives for Item 1

Alternatives	f	%
A) Gas pressure is downward.	5	4,8
B) Gas particles are getting smaller during the transition from the state of gas to liquid or liquid to solid.	6	5,8
C) There are almost non-existing forces between gas particles (*Correct Alternative)	72	69,2
D) Gases occupy different volumes according to their molecular weights.	14	13,5
E) Gas pressure depends on type of the gas particles and number of atoms contained in the gas.	7	6,7
Total	104	100

2. Which one of the following is not true about a substance in a closed container with gas remaining?

Table 2. Students' Selection of Alternatives for Item 2

Alternatives	f	%
A) The unit number of particles per square centimeter of container surface at the time of unit is the same.	5	4,8
B) The pressure of the gas is the same all over the walls of the container.	13	12,5
C) The pressure measured at any point in the vessel is the pressure of this gas.	5	4,8
D) The pressure inside the container is higher than the pressure made on the side surfaces of the pressure (*Correct Alternative)	75	72,1
E) The total number of collisions the particles have made with each other is equal to the total number of collisions they have made with the walls.	6	5,8
Total	104	100,0

72% of the students gave correct responses to this question and there was no misconception.

3. If a balloon inflated with a little puffing and mouth is connected to the balloon by taking it from its environment and putting it in the following media, it is expected to decrease the volume of the balloon?

Table 3. Students' Selection of Alternatives for Item 3

Alternatives	f	%
A) At the same pressure, colder (*Correct Alternative)	60	57,7
B) At the same pressure, warmer	28	26,9
C) At the same temperature, the temperature is higher	1	1,0
D) At the same temperature, the air is discharged	8	7,7
E) At the same altitude, warmer	4	3,8
No answer	3	2,9
Total	104	100,0

58% of the students gave correct responses to this question but 27% of the students had a misconception. In the category of temperature-gas volume, students hold the misconception of "In gas, volume and temperature are inversely proportional".

Birinci Konur and Ayas (2010) asked "Describe the change that can be observed at a normal inflated balloon, first in a cold environment, then in a warm environment by drawing" 14% of the students answered this question correctly by making drawings and explanations. 50% of the students made drawings and tried to explain this question only with pressure or by volume. 18% of the students briefly explained the situation without drawing at all. 15% of the students answered this question with misleading and conflicting expressions:

- In a cold environment the balloon remains swollen. It expands and shrinks in hot weather.
- When the balloon is warm, it becomes thicker and heavier. That's why it swells.
- In cold conditions the air molecules condenses and the balloon becomes bigger. In the hot air, it shrinks.
- When the balloon is in a warm environment, the volume decreases and the pressure increases.

4. The distribution of hydrogen gas molecules in a closed container at 25°C and 1 atm pressure was given in the picture (The circles (o) represent the distribution of hydrogen molecules). Which of the following diagrams illustrate the distribution of H_2 molecules when the temperature of the container is lowered to -15 ^{0}C? (Note: Before responding to this problem students were told that at -15 ^{0}C hydrogen is still gas.)

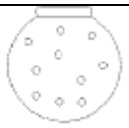
Item 4 was a conceptual problem and measured whether the gas particles expand when heated, and shrink when cooled. It is based on the knowledge that whatever the temperature, a gas will always occupy all the space available (Niaz, 2000).

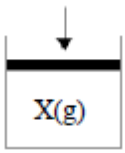
The percentages of students' selection of alternatives for item 4 were represented in Table 5. As seen from this table, only 1% of the students answered this question correctly.

However, 30 % of students chose the alternative B as a correct answer, indicating that they still had the misconception that when the gas in the container is cooled, each of the gas particles shrinks or gets smaller (Brook et al., 1984; Novick & Nussbaum, 1981; Sanger et al., 2000). Moreover 29 % selected alternatives D and E representing when the gas is cooled, gas particles started to accumulate at the bottom of the container like liquids. This misconception is in the category of temperature-gas molecule relationship, students hold the misconception

of "As the temperature increases, the volume of gas molecules expands for volume increase" (Karslı & Ayas, 2013).

Table 4. Students' Selection of Alternatives for Item 4

Alternatives	f	%
A  *Correct Alternative	1	1,0
B 	31	29,8
C 	12	11,5
D 	30	28,8
E 	30	28,8
Total	104	100,0



5. At constant temperature, the ideal gas X is placed in a piston chamber and the piston is compressed. Which of the following judgments about this gas at the end of the compression process is wrong?

Table 5. Students' Selection of Alternatives for Item 5

Alternatives	f	%
A) Pressure increases.	13	12,5
B) The distance between the particles decreases.	5	4,8
C) Increase the number of particles in the unit volume.	51	49,0
D) The mean velocity of the particles decreases (*Correct Alternative)	23	22,1
E) The number of particles does not change	12	11,5
Total	104	100,0

22% of the students gave correct response to the item 5. On the other hand 49 % of the students chose the alternative C because they thought that when the gases compressed, the number of gas particles in the unit volume increases.

6. When a constant-volume closed container filled with a gas is heated, increase in pressure is observed. In which of following alternative explains the reason of this event most accurately?

Item 6 was asked to explain the reason for the increasing pressure of gas when the gas is heated in a constant-volume container. It refers to the internal properties of the gases namely the relationship between molecular collisions and the pressure exerted by the gas (Niaz, 2000). As Table 7 indicates, 37% of the students selected the scientifically correct response as stating that when the gas is heated in a constant-volume container, the number of collisions increase so do the pressure. However, 23% of the students considered that when the gas is heated, the size of the of gas particles increases (Alternative A). In addition, 21 % of students believed that when the gas is heated in a constant-volume container, gas particles condense in the wall of the container (Alternative E). These students conceptualize the increase in pressure of a gas as a product of both the expansion of the molecules (leading to repulsive forces) and the faster speed (Niaz, 2000) that make the molecules hit the walls of the container and condense in there.

Table 6. Students' Selection of Alternatives for Item 6

Alternatives	f	%
A) Increase the size of gas particles	24	23,1
B) Increase in the numbers of particles when the gas is heated	11	10,6
C) Becoming heavier of the gas when it is heated	9	8,7
D) Increase in the number of the collisions when the gas is heated (*Correct Alternative)	38	36,5
E) When the gas is heated, gas particles condense in the wall of the container.	22	21,2
Total	104	100,0

7-9

A constant-volume container filled with air is placed into a bath and connected to a computer. Temperature changes are followed by a thermometer placed. Moreover, container is connected to device for measuring pressure and pressure can be read on the computer. The temperature of the bath is 25 °C and the pressure is 1 atm.

7. Which of the following diagrams shows the distribution of molecules that form the air at 25 °C within the container the best?

Table 7. Students' Selection of Alternatives for Items 7-8

Alternatives	Item 7		Item 8		Item 9	
	f	%	f	%	f	%
A 	6	5,8	7	6,7	46	44,2
B 	1	1,0	9	8,7	34	32,7
C 	7	6,7	36	34,6	2	1,9
D  *Correct Alternative	89	85,6	2	1,9	14	13,5
E 	1	1,0	50	48,1	8	7,7
Total	104	100,0	104	100,0	104	100,0

About 86% of the students gave correct responses to this question. There was no misconception

8. The temperature of the container is reduced to 0 °C by adding ice into bath. After waiting to affect the temperature change on air particles, which of the following diagrams shows the distribution of molecules within the container the best? (Note: Before responding to this problem students were told that at 0 ^{o}C air is stil gas.)

Similar to item 4, item 8 was a conceptual problem measuring the distribution of air in a constant-volume closed container when decreasing the temperature of the container. In addition, before responding to this problem, students were informed that at 0 ^{o}C air is still gas. The percentages of experimental and control group students' selection of alternatives for item 8 was presented in Table 9. Results indicated that only 2% of the students selected this

scientifically correct answer, which represents the homogeneous distribution of air with decreasing temperature. On the other hand, 83% of the students believed that gas particles are unevenly scattered in any enclosed space and (35% thinks air molecules accumulated at the bottom of the container while 35% thinks the particles accumulate in the middle of the Erlenmeyer with decreasing temperature as figured out in alternatives E and C.

9. The temperature of the container containing gas is increased to 60 °C by heating the water bath with the help of heater. In this case, which of the following diagrams shows the distribution of molecules within container the best?

Item 8 and item 9 were the sequential questions having the same question root. Item 9 was asked to measure the distribution of air molecules in a constant volume container with increasing temperature. The percentages of students' selection of alternatives for item 9 was provided in Table 10. Scientifically correct answer, figured in alternative D, was the homogeneous distribution of air molecules even if the temperature is increased, and only 14% of the students gave correct responses to this question. When the students' responses were examined for each alternative, the frequency of selecting alternative A draws the attention. In other words, 44% of the students believed that gas particles are unevenly scattered in any enclosed space and air molecules accumulates on the walls of the container with increasing temperature. Similarly, 33% of the students thought that with increasing temperature air molecules rises and accumulates at the top of the Erlenmeyer. This misconception is in the category of temperature-gas volume, students hold the misconception of "As the gas molecules in the closed container are heated, the molecules are collected above the container" or "When gas molecules in a container are heated, they move up the container to reduce the density" (Karslı & Ayas, 2013

Birinci Konur & Ayas (2010), when asked 'what do you think about the movement and distribution of gas molecules in the closed syringe when it is heated? What do you think about the movement and distribution of gas molecules in the closed syringe when it is heated? To the classroom teacher education students, 24% of the students made incorrect drawings and misleading statements. According to these students, "The gas molecules on the side where the heat is applied slide to the other side, so they move to the right side" and "Gas molecules rise and shrink under the influence of heat".

10. A container filled with air is connected to a balloon as shown in the figure. When the tap of the container is opened and the container is heated, it is observed that balloon is swelling. Which of the following illustrate the distribution of air the best after swelling the balloon? (Dots (.) represent the molecules within air.)

Related to item 9, item 10 aimed to investigate the distribution of air molecules when the constant-volume container connected to a balloon as shown in the figure in Table 11 is heated. The percentages of students' selection of alternatives for item 10 were indicated in Table 11. Scientifically correct answer was given in alternative C showing the homogeneous distribution of air within the container and the balloon even if the container was heated. Results indicated that only 20 % of the students were aware of the homogeneous distribution of gases when the tap of the container connected to balloon is opened and the container is heated simultaneously.

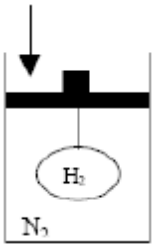
On the other hand, 70 % of the students though that Gas particles are unevenly scattered in any enclosed space and Gas particles rise and stay away from heat (alternatives B, D, and E). 30% selected alternative D repeating the misconception that hot air increases. These results of Item 10 supported the results of the item 9 in terms of raised hot air towards

the top of the container and the accumulation of gas molecules on the walls of the container with increasing temperature. Additionally, 18 % of the students selected the figure given in alternative B, which means they believed that some of the heated air accumulated on the walls of the balloon. Furthermore, 25 % of students thought that when the tap between the container and balloon is opened, most of the air molecules or all of them are transferred to the balloon. This misconception is in the category of temperature-gas volume, students hold the misconception of "As the gas molecules in the closed containers are heated, the molecules are collected above the container" (D and E) (Karslı & Ayas, 2013). A similar question was asked to science teacher education students and although at least 5% of the students drawed the same number of particles in the both parts correctly; at least 18% of the students drawed more particles in the second part and less particles in the first part (Çavdar et al., 2016). Since the students drawed more particles in the second part, they thought that the number of particles increases with the temperature increase and when the particles increase in the number so does the volume (Çavdar et al., 2016).

Table 8. Students' Selection of Alternatives for Item 10

Alternatives	f	%
A 	9	8,7
B 	19	18,3
C  ***Correct Alternative**	21	20,2
D 	29	27,9
E 	26	25,0
Total	104	100,0

11. As shown in the figure, nitrogen gas is found in the cylindrical container with movable frictionless piston. Hydrogen gas is found in the elastic balloon connected to cylinder by a steel rope. If the cylinder is pushed downward without touching of elastic balloon to the surface of the vessel, what will be the shape of balloon?



Item 11 was about the effect of changing pressure on an elastic balloon, the related figure was given in the Table 12. Scientifically correct answer was the increasing of pressure inside the non-constant volume container when movable frictionless piston is pushed towards the downward. Since the gases distributes homogenously wherever they are placed, the balloon inside the container shrinks from everywhere by the effect of increased pressure on it. The percentages of students' selection of alternatives for item 11 were represented in Table 12. 46 % of students answered this question correctly. However, 20 % of students' selected alternative A and thought that when movable frictionless piston is pushed towards the downward, the elastic balloon explodes. In fact, they may think that when the pressure drops on the balloon, its volume increases and so it explodes. One of the reasons of selecting this alternative might be the daily life experiences because if someone compresses the balloon from one or two sides, it generally explodes.

Table 9. Students' Selection of Alternatives for Item 11

Alternatives	**f**	**%**
A) Balloon explodes.	21	20,2
B) Balloon shrinks only from both sides.	10	9,6
C) Only upper part of the balloon shrinks.	16	15,4
D) Only the bottom of the balloon shrinks.	8	7,7
E) Balloon shrinks from everywhere. (*Correct Alternative)	48	46,2
No answer	1	1,0
Total	104	100,0

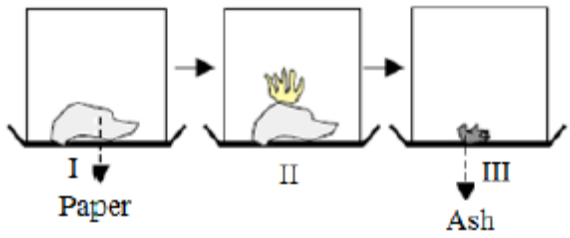
12. What exists between the particles of a gas?

Item 12 was intended to ask what the students think about what exists among the particles of a gas. Since gas particles cannot be seen by naked eyes, two responses came from students. Scientifically correct answer should be "nothing" is found between the particles of a gas. The percentages of students' selection of alternatives for this item were given in Table 10. Only 14% of the students believed that there was nothing between the particles of a gas. On the other hand, 64% of the students believed that Matter, especially air, exists between the particles/atoms of a gas (Novick & Nussbaum, 1978, 1981) and chose the alternative A. One of the reason for choosing this option could be the finding of air in everywhere of the world. Therefore, they might think that air was found even within gas particles.

Table 10. Students' Selection of Alternatives for Item 12

Alternatives	f	%
A) Air	67	64,4
B) Water vapor	5	4,8
C) Other gases	13	12,5
D) Nothing (*Correct Alternative)	15	14,4
E) Foreign substances (dust, dirt, etc.)	4	3,8
Total	104	100,0

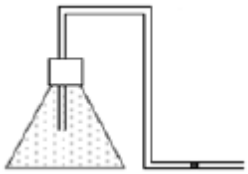
13. As shown in following figure, a piece of paper is put in a glass container in condition I. In condition II paper is burning and in condition III ash is formed. In all three cases, glass container is weighted. Accordingly, which one of the following is true?



Item 13 was about the conservation of the mass of a gas. Law of conservation of matter was First clearly stated by 18th-century chemist Antoine Lavoisier. This law describes that in a closed system, matter is neither created nor destroyed. Atomic theory means that all matter is composed of elements made from indestructible particles called atoms. It explains why matter is conserved in chemical reactions (Maeng & Bell, 2013). As shown in Table 11, a piece of paper is put in a closed glass container and left to burn. Glass container is weighted before burning, during the burning and after burning. The total mass stays the same because of the closed container. Therefore, scientifically correct answer was the equality of mass of each container actually depending on the law of conservation of mass. The percentages of students' selection of alternatives for item 13 were presented in Table 11. 29 % of the students answered this question as correct. On the other hand, 64% of the students though that gases have no mass (Stayv, 1987 as cited in Morgil, Erdem, & Yılmaz, 2003); gases weight can be ignorable; conservation of matter applicable to solids and liquids but may be ignored for gaseous reactants or products; (27 % of students believed that container has the biggest mass in condition I and chose the alternative A whereas 24 % of students thought that the closed container has the biggest mass in condition II and chose the alternative B).

Table 11. Students' Selection of Alternatives for Item 13

Alternatives	f	%
A) Condition I has the biggest mass	28	26,9
B) Condition II has the biggest mass	25	24,0
C) Condition III has the biggest mass	11	10,6
D) I and II has the same weight and III is less	10	9,6
E) All of them have the same mass (*Correct Alternative)	30	28,8
Total	104	100,0



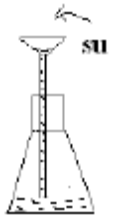
14. In the system, there is a drop of mercury in the glass container. The mercury drop moves to the right or left depending on the pressure and temperature change inside the glass container. If the apparatus of the room temperature (25 ^{o}C) is taken to an environment 5 ^{o}C, which of the following is correct regarding to the movement of the mercury?

In item 14, the pressure of glass container containing mercury was changed by changing the temperature of its environment. It was expected from students to predict the direction of the mercury drop depending on the pressure change of the given system. As seen from the Table 12, only 26% of the students gave correct answer by stating the way of movement as a result of decreasing pressure within the container with decreasing temperature. On the other hand, 34% of the students selected alternative D. They considered the direction of the mercury droplet to the right since pressure inside the container decreases due to decrease in temperature and increase in volume. Although the glass container was specified, these students considered the change in the volume of the system since the pressure inside the container decreases. To think "In a closed container, the volume of a gas decreases when the temperature decreases" is a Misuse of Charles's law (the direct relationship between the temperature and volume of a gas) ((Maeng & Randy Bell, 2013). This misconception is in the category of temperature-gas volume, students hold the misconception of "In gas, volume and temperature are inversely proportional" (Karslı & Ayas, 2013).

Table 12. Students' Selection of Alternatives for Item 14

Alternatives	f	%
A) Remain moveless because air pressure is constant.	21	20,2
B) First it moves to left, and then it moves to right.	3	2,9
C) Moves to the left, the pressure decreases within the container with decreasing temperature (*Correct Alternative)	27	26,0
D) Moves to the right, the pressure inside the container decreases with decreasing temperature and volume increases.	35	33,7
E) Moves to the right, with/in decreasing temperature volume decreases and pressure of the container increases.	17	16,3
No answer	1	1,0
Total	104	100,0

15. According to the figure given on the right, the container connected to a funnel is closed with a stopper preventing the gas leak from the container. Water is easily entered when poured to the container but when the water level in the container is reached to the bottom of the funnel, water input is becoming difficult. What is the reason of this event?



Nearly 57 % of the students gave correct responses to this question. On the other hand, 31% of the students though that The existence of the gas can be ignorable in a closed container when there is some amount of liquid in it (Misuse of Boyle's law) and chose the alternative D. Boyle's law describes the relationship between the pressure and volume of a gas under relatively normal conditions (close to room temperature and pressure). Boyle's law states that, when holding temperature constant, the pressure of a gas is inversely proportional to its volume (Maeng & Bell, 2013).

Table 13. Students' Selection of Alternatives for Item 15

Alternatives	f	%
A) The water inside the pot closes the inlet and no water can enter.	4	3,8
B) If the pot was bigger, it would get more water.	1	1,0
C) Increased internal pressure prevents water ingress (*Correct Alternative)	59	56,7
D) The water inside the pot is applying upward pushing force and water cannot enter.	32	30,8
E) The lifting force of the water has become unable to remove more water.	8	7,7
Total	104	100,0

16.

At constant temperature and pressure, the piston of the syringe containing an amount of air (condition 1) is pushed a bit and the air inside is compressed (condition 2). What is true about the gas particles forming air after compression?

About 79% of the students gave correct responses to this question. There is no misconception.

Table 14. Students' Selection of Alternatives for Item 16

Alternatives	f	%
A) The particles stick together.	3	2,9
B) All the particles are collected on the tip of the syringe.	10	9,6
C) The particles shrink.	3	2,9
D) The distance between the particles decreases. (*Correct Alternative)	82	78,8
E) Particles burst due to high pressure.	5	4,8
No answer	1	1,0
Total	104	100,0

17. At a constant temperature, during the transition of a pure matter in the phase of solid to liquid or liquid to gas, which of the following features of particles will change?

I. Size

II. Average Kinetic Energy

III. The distance between particles

Item 17 was related to the interpretation of what features of particles change during the transition of a pure matter in the phase of solid to liquid or liquid to gas at constant temperature. The correct answer was only the changing of distance between the particles during the transition of a pure matter in the phase of solid to liquid or liquid to gas. Size of the particles cannot change whether the temperature increased or decreased. In addition, average kinetic energy does not change unless there is any change in temperature. Results presented in Table 15 indicated that 22 % of students answered the question correctly by stating that the distance between particles will change during the phase transition. In contrary to this result, 65 % of the students thought that size of the particles, average kinetic energy and the distance between particles change in case of phase changes. This misconception is in the category of temperature-gas molecule relationship, students hold the misconception of "The kinetic energy between the gas molecules increases as the temperature decreases" (E) (Karslı & Ayas, 2013)

Table 15. Students' Selection of Alternatives for Item 17

Alternatives	f	%
A) Only I	0	0
B) Only II	2	3
C) Only III (*Correct Alternative)	3	23
D) I and III	4	10
E) I, II and III	5	68
Total	Total	104

18. Which of the following statements is wrong about gases?

Item 18 was also related with the properties of gases. Table 16 representing the percentages of students' selection of alternatives for this item indicates that 48% of students believed that diffusion rate of gases decreases with increasing molecular weight at the same temperature. On the other hand, a significant part of students (43%) thought that average kinetic energy of the all gases is not equal at the same temperature and chose the alternative D.

Table 16. Students' Selection of Alternatives for Item 18

Alternatives	f	%
A) They have a particulate structure.	3	2,9
B) Gases are distributed homogeneously in the container in which they are present.	1	1,0
C) Gas pressure depends on the number of particles in unit volume.	5	4,8
D) At the same temperature, average kinetic energy of all gas is the same.	45	43,3
E) At the same temperature, when the molecular weight of gases increases their rate of diffusion increases (*Correct Alternative)	50	48,1
Total	104	100,0

19. About the properties of cold and hot air which of the following statements is true?

Item 19 was related to the properties of cold and hot air. As presented in Table 17, 12% students selected the correct alternative stating that hot and cold air may have different volumes but they have equal masses. On the other hand, 75% of the students though that Air neither has mass nor can it occupy space and chose the alternatives A and E (50% students believed that while hot air particles expand, the cold air particles shrink; 25% students had the common misconception that hot air has little mass and is lighter than cold air). This misconception is in the category of temperature-gas molecule relationship, students hold the misconception of "As the temperature increases, the volume of gas molecules expands for volume increase" (Karslı & Ayas, 2013).

Table 17. Students' Selection of Alternatives for Item 19

Alternatives	f	%
A) Hot air is lighter than cold air.	26	25,0
B) Hot air is heavier than cold air.	9	8,7
C) Air has neither a mass nor a volume either hot or cold does not matter.	5	4,8
D) Hot and cold air may have different volumes but they have equal masses (*Correct Alternative)	12	11,5
E) Hot air gas particles expand while cold air particles shrink.	52	50,0
Total	104	100,0

20. The pressure of a balloon filled with air is measured as P_{full} in an environment where the pressure of atmosphere is P_{atm}. The balloon's mouth is opened and expected to shrink, and the pressure of collapsed balloon is measured as $P_{colllapsed}$. Which of the following is correctly related the pressures of P_{atm}, P_{full} and $P_{collapsed}$?

Table 18. Students' Selection of Alternatives for Item 20

Alternatives	f	%
A) $P_{collapsed} < P_{atm} < P_{full}$	40	38,5
B) $P_{collapsed} = P_{atm}$, $P_{atm} < P_{full}$	17	16,3
C) $P_{atm} = P_{full} = P_{collapsed}$ (*Correct Alternative)	4	3,8
D) $P_{atm} > P_{full}$, $P_{collapsed} = 0$	25	24,0
E) $P_{atm} < P_{full}$, $P_{collapsed} = 0$	15	14,4
No answer	3	2,9
Total	104	100,0

About 4% of the students gave correct responses to this question and stated that "hot or cold air has different volumes but same mass" is correct. On the other hand, 63 % of the students though that "Deflated balloon has less pressure inside than outside" and "The pressure of air inside the balloon is different from the pressure outside" and chose the alternatives A (39 %) and D (24 %).

21. Which of the following statements about the properties of gases is wrong?

Another question about the properties of the gases was the item 21. As seen from the Table 19 below, a large part of the students (97%) know that gases are not located at the bottom of the container when they are placed in a closed container and gave correct responses to this question. There is no misconception.

When Birinci Konur and Ayas (2010) studied the gas molecule drawings of classroom teacher education students in order to determine how the students constructed the gas concept in their minds, they realized that 34% of the students made accurate explanations about gas molecules and drawings supporting these explanations. In the explanations made about these drawings, students used the expression "The gas molecules are homogeneously dispersed evenly in the container".

Table 19. Students' Selection of Alternatives for Item 21

Alternatives	f	%
A) Gases can be liquefied.	1	1,0
B) Gas particles are constantly in motion.	0	0
C) When gases are placed in a container, gas particles are located at the bottom of the container as liquids (*Correct Alternative)	101	97,1
D) The forces between gas particles are weak as almost none existing.	2	1,9
E) Gas particles move randomly, there is no certain order of movement.	0	0
Total	104	100,0

22. A balloon made from rubber is filled with hydrogen gas and the mouth of it is tightly connected. However, after a few days later it is observed that balloon collapses. Which of the following best explains this situation?

In item 22, students were asked the reason to explain for collapsing of a balloon though its mouth was tightly connected. The scientifically correct answer is the escaping of gas from the pores of the balloon. As seen from Table 20 below, 14 % of students answered this question correctly. 32% students believed that increased external pressure was the reason of decreasing the volume of the balloon. However, in order to change the external pressure on balloon, it should be taken to a location having different altitude and in item 22 there was no information about change in external pressure. In addition, 34 % of students believed that weather is cooled and the molecules in balloon were clustered due to it. Cooling of weather might be the reason of shrinking or decreasing the volume of the balloon but the molecules in the balloon cannot be clustered somewhere upon cooling of weather which is the common misconception found in literature (Novick & Nussbaum, 1981).

Table 20. Students' Selection of Alternatives for Item 22

Alternatives	f	%
A) External pressure increases and the balloon gets smaller.	33	31,7
B) The molecules inside the balloon are getting smaller as a result of collisions.	6	5,8
C) The weather cools and the molecules in balloon are clustered.	35	33,7
D) Energy of molecules dissipated in time and their movements stop.	15	14,4
E) The gas escaped from the pores of the balloon (*Correct Alternative)	15	14,4
Total	104	100,0

23. In the ideal behaviour of X_2 and X_3 gases' temperature, volume and number of molecules are equal. Which of the following comparison is wrong about these gases?

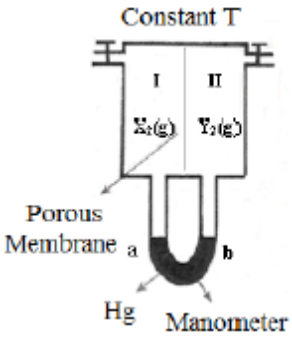
Item 23 was the one of the 1996 university entrance exam questions in the subject of chemistry in Turkey. This item aimed to make students use ideal gas law for two different gases containing the same kind of atoms. As seen from Table 21 below, 36 % students thought that pressures of X_2 and X_3 gases are equal. However, 43% of the students misused the ideal gas law: 23 % students selected alternative D and thought that these gases have different numbers of moles though the equality in number of molecules was mentioned in item 23. So, the problem with the mole concept was clearly seen in this question. What is more, 20 % of the students chose alternative E and considered the average kinetic energy of these two gases as being different. These students were not aware of the fact that average

kinetic energy of the gases depends on the temperature and at the same temperature, the average kinetic energy of gases are the same.

Table 21. Students' Selection of Alternatives for Item 23

Alternatives	f	%
A) Pressures are different (*Correct Alternative)	37	35,6
B) Densities are different	12	11,5
C) Masses are different	10	9,6
D) The same number of moles	24	23,1
E) The same average kinetic	21	20,2
Total	104	100,0

24. As shown in figure, a container is separated into compartments I and II with a porous membrane and connected to a manometer. Being equal the levels of mercury in the arms of the manometer, compartment I is filled with X_2 gas and compartment II is filled with Y_2 gas. At the same temperature, after a short period of time it is observed that the level of mercury in arm "a" increases.



According to this observation, about the X_2 and Y_2 gases,

I. X_2 molecules are faster than Y_2 molecules.

II. Molar mass of Y_2 is more than that of X_2.

III. During the observation, total pressure of compartment II is increased.

Which of the above statements is true?

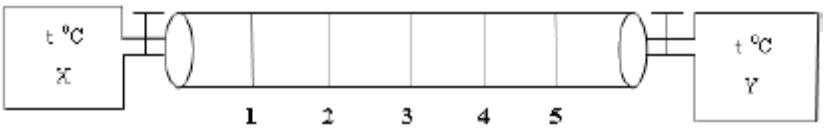
Item 24 aimed to make the students think about both diffusion of gases through a porous membrane and gas laws. The reason for increasing mercury level in arm "a" is due to the increase in pressure in compartment II. Since the volume and temperature are equal for compartment I and II, changes in the number of moles is the only reason for pressure change. Both X_2 and Y_2 gases passes through a porous membrane but X_2 gas should be faster than Y_2 gas in order to increase the pressure of compartment II. That is, diffusion rate of X_2 is bigger than the Y_2. Therefore, it can be concluded that since the temperature is equal, molecular weight of X_2 is smaller than Y_2. As the Table 22 below reveals, 14 % of students answered this question correctly.

On the other hand, 42% of the students selected alternative D, these students think that diffusion rate of gases increases with increasing molecular weight and did not think about the possibility of diffusion of the gases through the porous membrane.

Table 22. Students' Selection of Alternatives for Item 24

Alternatives	f	%
A) Only I	16	15,4
B) Only II	15	14,4
C) I and III	13	12,5
D) II and III	44	42,3
E) I, II and III (*Correct Alternative)	14	13,5
No answer	2	1,9
Total	104	100,0

25.



As shown in figure, X and Y gases are left to diffuse toward each other and as they come across at the 5th section of the tube,

I. The diffusion rate of X is more than Y.

II. Molecular weight of X is more than Y.

III. The container in which Y gas is found must be heated for encountering of both gases in the middle of the tube.

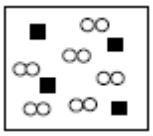
Which of the statement(s) is true?

Unlike item 24, item 25 was a kind of question often encountered in textbooks about the diffusion of gases. X and Y gases with same temperature were left to diffuse toward each other and met at the 5th section of the tube. As seen from the Table 23 below, 23 % of students did answer the question correctly. 59 % of the students could not establish the connection between molecular weight and diffusion rate (alternative E) and though that diffusion rate of gases increases with increasing molecular weight.

Table 23. Students' Selection of Alternatives for Item 25

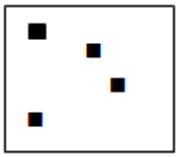
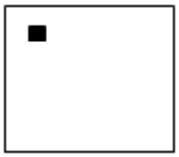
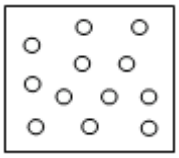
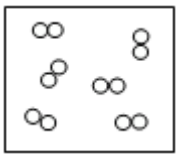
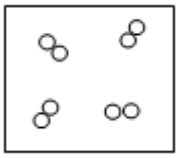
Alternatives	f	%
A) Only I	3	2,9
B) I and II	10	9,6
C) I and III (*Correct Alternative)	61	58,7
D) II and III	6	5,8
E) I, II, III	24	23,1
Total	104	100,0

26. The following closed container, as shown in picture, contains a mixture of oxygen (∞) and helium (■) gases at 25 ^{o}C. Which one of the following is the partial pressure of the oxygen gas?



Item 26 is related to the partial pressure concept of gases. A mixture of oxygen and helium gases was figured in a closed container and students are asked to select the figure that represents the partial pressure of oxygen gas. As Table 24 indicates, 60% of the students gave the correct response by selecting the container including only oxygen molecules (alternative D). However 21% of the students thought the partial pressure of oxygen gas as the homogenously distributed oxygen atoms, not the molecules and decided to choose the figure given in alternative C. This is a misconception that conceptual calculations are not obvious for students.

Table 24. Students' Selection of Alternatives for Item 26

Alternatives	f	%
A 	4	3,8
B 	0	0
C 	22	21,2
D  (*Correct Alternative)	62	59,6
E 	15	14,4
No answer	1	1,0
Total	104	100,0

4. DISCUSSION

In this study, classroom teacher education students' understanding of gas concepts was measured by a multiple-choice test. The proportions of correct responses in this test were determined by item analysis. It was found that students had misconceptions on some gas concepts:

Gas particles are able to "shrink", "condense", "sink", or "settle" (Novick & Nussbaum, 1981).

Air exists among the particles of a gas (Novick & Nussbaum, 1978 as cited in Yalçınkaya, 2010). In addition, most of them ignored the mass of gases (Lee et al., 1993 as cited in Yalçınkaya, 2010; Mas, Perez, & Harris, 1987; Stavy, 1988 and 1990 as cited in Yalçınkaya, 2010).

The size of the particles increases from the state of solid to liquid or liquid to gas.

In a closed container, when the gases are cooled, gas particles are accumulated in the middle of it.

The size of the gas particles decreases with increase in temperature.

Gas particles become heavier due to heat taken.

Students have difficulty in conceptual understanding of partial pressure.

In a closed container, gases do not exert the same pressure in different directions.

Gas particles are unevenly scattered in any enclosed space" (Novick & Nussbaum, 1981; Lee et al., 1993 as cited in Yalçınkaya, 2010; Cho, Park, & Choi, 2000),

Matter, especially air, exists between the particles/atoms of a gas" (Novick & Nussbaum, 1978 as cited in Yalçınkaya, 2010, Novick & Nussbaum, 1981; Lee et al., 1993 as cited in Yalçınkaya, 2010),

Conservation of matter is applicable to solids and liquids but may be ignored for gaseous reactants or products" (Mas, Perez, & Harris, 1987),

In a closed container, the volume of a gas decreases when the temperature decreases (Misuse of Charles's law)" (Lin, Cheng, & Lawrenz, 2000),

Conceptual calculations are not obvious for students" (Nurrenbern & Pickering, 1987; Sawrey, 1990; Nakhleh & Mitchell, 1993),

Molecules increase in size with change of state from solid to liquid to gas" (Haidar & Abraham, 1991 as cited in Yalçınkaya, 2010),

Gas particles sink to the bottom of the container when the temperature is lowered",

Gas particles may condense on the walls of the container" (Novick & Nussbaum, 1981), Heated or hot air weighs more than cold air or vice versa" (Lee et al., 1993 as cited in Yalçınkaya, 2010),

When the air is compressed, the particles stick to each other",

Misuse of ideal gas law" (Lin, Cheng, & Lawrenz, 2000),

If the volume decreases, the speed of the particles increases due to the increase in the number of collisions" (Kautz, Heron, Shaffer, & McDermott, 2005), and

Gases occupy different volumes according to their molecular weights" (Cho, Park, & Choi, 2000).

In students, the existence of alternative concepts in pressure-volume relationship and temperature-volume relation in gas is determined. In order for these alternative concepts to be formed, it is necessary that students do not fully understand the meaning of the PV = nRT formula and that this connection is used inappropriately (Bak et al., 2008; Kautz, Heron, Shaffer, & McDermott, 2005; Karsli, 2011; Lin, Cheng, & Lawrenz, 2000). However, it can be shown that students who are involved in temperature-changing, position, and movement of gas molecules in a trap under the temperature-gas molecule relationship category have alternative concepts, that preliminary learning about the properties of gases is inadequate and superficial, or that the invisibility of gases prevents students from forming a gas concept (Stavy, 1988 as cited in Yalçınkaya, 2010), or in other words, they may not be able to visually perceive gas behaviour. All of these reasons are a consequence of the students' inability to perceive the kinetic theory used to explain the behaviour of gases at the conceptual level.

Using simulation applets in comparison to traditional didactic, chalk-and-talk instruction facilitates understanding of gas pressure concepts as well as the positive attitudes ot the students towards the use of the simulation applets (Oh, Treagust, Koh, Phang, Ng, Sim, & Chandrasegaran, 2012).

For the students to understand the concept of gas pressure, it is necessary to know the properties of the molecular structure of gases and the behavior of these molecules in a molecular way. In other words, students need to know Kinetic Molecular Theory, which explains the properties of gases, such as pressure, temperature, volume, depending on their molecular composition and motion (Şahin & Çepni, 2012). According to Kinetic molecular theory, Matter consists of tiny particles in constant motion, whose speed is proportional to the absolute temperature. It Explains gas laws.for example, explains the relationship expressed by Boyle's law in terms of gas particle motion. It also explains Charles's law (the direct relationship between the temperature and volume of a gas) ((Maeng & Randy Bell, 2013).

5. IMPLICATIONS

This study has several important implications for classroom teachers, educators, and researchers:

Gas concepts are been used in daily life so there are many conceptions about gases in students' mind before instruction. While some of them are true, some of them conflict with scientific knowledge. Pre-service teachers have some misconceptions on gas concepts and these can be passed to their students when they become a teacher.

Teacher educators should take in consideration misconceptions while designing their lessons. Faculty of education should open more courses dealing with the misconceptions and these courses should include strategies help pre-service teachers to remedy them in their subject area.

Teacher educators should organize workshops organized by the University and the Ministry of National Education to primary or secondary school teachers about new teaching techniques. And teachers should be trained and be encouraged to use new teaching techniques in order to enrich their lessons.

Researchers should determine the misconceptions on the students and teachers and work for the effective methods of teaching to overcome those misconceptions. More importance should be given to conceptual change strategies in order to make student misconceptions appear. The gas concepts should be represented with using macroscopic, symbolic and microscopic states in harmony so that the concepts should be constructed easily by students. In this regard computer aided instruction and mobile technologies should be used to visualise these states.

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THE CHALLENGES OF TEACHING PRACTICE OF UNDERGRADUATE MATHEMATICS STUDENTS[*]

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ABSTRACT

*A **p**edagogical formation education certificate program is a training program that enables the 4-th grade students of the mathematics department of the science and literature faculty to qualify for the teaching certificate required to become a teacher. The students of Niğde Ömer Halisdemir University mathematics department participates in the course that the education faculty have prepared. In this program, for the practice teaching course, the students spend 2 hours of theory at the faculty and 6 hours of practice in a high school in Niğde city center. The lecturer observes that the students who are carrying out the theoretical part of the course are deficient in the use of tools and materials, are inadequate in preparing the lesson plan, lack of mastery of the subject and lack of skills in using the board: teachers in the application notes that teacher candidates have difficulties in communication with high school students. The purpose of this study is to explain what the formation students think about difficulties encountered by them in in the practice school. It is believed that this study will help students to develop their skills on weekly basis in an activity file that will be prepared in the form of lectures, lesson planning, classroom dominance, appropriate use of equipment.*

1. INTRODUCTION

Consisting of cognitive, emotional and psychomotor skills, teaching is a profession where social skills are at the forefront. It is multi-dimensional and rich knowledge and experience (Karadüz, Eser, Şahin & İlbay, 2009). Individuals preparing for this profession must have acquired a lot of cognitive knowledge and skills before starting the profession and must have developed positive attitudes and behaviors (Karadüz, Eser, Şahin & İlbay, 2009). The individual skills of the individuals preparing for the teaching profession are shaped by undergraduate major area courses and the theoretical and practical knowledge provided in educational science courses (Karadüz, Eser, Şahin & İlbay, 2009). Coming at the forefront of the vocational education practices, Teaching Practice is the course that includes practices and activities related to the profession, that students acquire the skills and experience required in the profession pre-service and that the students develop opinions and views about the

[*] This study is the revised version of the same name paper presented in the "2nd International Rating Academy Congress: Hope" held in Kepez / Çanakkale on April 19-21, 2018.

profession (Karadüz, Eser, Şahin & İlbay, 2009). Since Teaching Practice provides the students with the applicable knowledge and skills related to the profession, the importance should be given to the practical part of the course (Karadüz, Eser, Şahin & İlbay, 2009). In this respect, the practices of this course should be carried out without interruption, and the interactions of the teacher candidates in the learning environments should be enriched (Karadüz, Eser, Şahin & İlbay, 2009). Encountering many problems during the practices in the practice school, the teacher candidates try to determine the problems and solve them (Karadüz, Eser, Şahin & İlbay, 2009). The candidate teachers will make sense of what they learn and interpret them as they face these events and situations (Karadüz, Eser, Şahin & İlbay, 2009).

The studies conducted on this subject suggest that the practices are necessary for the development of teacher candidates' teaching skills (Karadüz, Eser, Şahin & İlbay, 2009). Some studies argue that there are important disruptions and problems during practices (Karadüz, Eser, Şahin & İlbay, 2009). Problems that arise during practice negatively affect the development of the teacher candidates (Karadüz, Eser, Şahin & İlbay, 2009). Despite these negativities, it is necessary to include practical learning while preparing the students towards the teaching profession (Karadüz, Eser, Şahin & İlbay, 2009). Positive or negative views and attitudes developed by the students in the Teaching Practice course give information about the achievement level of the course (Karadüz, Eser, Şahin & İlbay, 2009). The students' opinions about the practice are important since they reflect student achievement as well as the effectiveness level of the course (Karadüz, Eser, Şahin & İlbay, 2009). Therefore, in this study, the difficulties of the students enrolled in the pedagogical formation certificate program encounter during the Teaching Practice in the practice school they went to and the reasons behind these difficulties were determined.

2. MATERIAL AND METHODS

In this study, the qualitative research model was employed. The qualitative model was preferred because it is related to the experiences of the individuals and their interpretation of these experiences (Orhan, 2010).

2.1. Study Group

The study group of the study is made up of Mathematics students enrolled in the pedagogical formation certificate program of Niğde Ömer Halisdemir University during the 2017-2018 academic year. The related instructor had 15 students in this Mathematics group. Ten of these students participated in the study. Teacher candidates participating in the research were determined on the basis of volunteerism.

2.2. Data Collection Tool

A semi-structured interview form was used as a data collection tool in the study. In order to develop the interview questions, the related literature was reviewed and the draft form was prepared. The developed draft form was presented to a specialist in the same department as the researcher for expert opinion. Bringing an outside opinion, expert opinion is useful in seeing, reviewing and presenting ideas that are not seen by the researcher. The interview question was revised in line with the expert opinion. Then, the semi-structured interview form was administered to ten teacher candidates who were in the Math pedagogical formation certificate program. When the answers given by the teacher candidates to the question were evaluated, it was concluded that the question served its desired purpose.

In the study, the answer to the following question was sought: What were the difficulties you encountered as a teacher candidate during Teaching Practice course?

2.3. Data Collection and Analysis

Data were obtained by administering the semi-structured interview form to the volunteer teacher candidates. The obtained data were analyzed by descriptive analysis. Descriptive analysis was preferred because the conceptual structure of the data obtained in the research was previously determined and the analysis was made based on the structure (Çepni, 2014). For this purpose, the categories made in the studies of Çiçek and İnce (2005) and Karadüz, Eser, Şahin and İlbay (2009) were used.

In the study, the analysis was made in light of the descriptive analysis stages given by Yıldırım and Şimşek (2003). Accordingly, the following steps were taken in the descriptive analysis conducted in this study: A framework was formed based on the research question, the questions were read and arranged according to the framework, the data were grouped together in a meaningful and logical way and were supported with direct quotations by identifying them.

During the analysis, the teacher candidates' real names were not used. In the study, by giving quotations from the teacher candidates' views, the validity was ensured. The reliability of the study was ensured by the data being categorized by two different researchers.

3. RESULTS AND DISCUSSION

In this section of the study, the data regarding the research question is presented in tables. In the first question of the study, the teacher candidates were asked the following question: What difficulties do you encounter during the teaching part of the practice as a teacher candidate? The undergraduate mathematics teacher candidates' views regarding this question are given in Tables 1-7.Figure 1 shows the absorption spectra for ROS and EZE and their mixture in methanol.

3.1. Difficulties Teacher Candidates Face about Communication

According to the data in Table 1, the greatest difficulty for teacher candidates about communication is not being able to feel comfortable while teaching. Nine of the teacher candidates stated that they feel nervous while teaching. Some of the answers these candidates have given are as follows:

"Teaching part of the practice is very stressful for me. Because of this, I can't be comfortable." (Kübra)

"I am too excited while I teach because I am afraid I won't be able to give what I know and I won't be helpful for the students because of my inexperience." (Merve)

"I am afraid that I won't be able to teach because of feeling nervous since I am inexperienced." (Sena).

Another difficulty teacher candidates face about communication is not being able to give clear instructions and directives. Three of the teacher candidates stated that they could not give clear instructions and directives. Some of the answers these candidates have given are as follows:

"During my teaching, I encountered small difficulties in the way that I wondered how I can transfer the difficult sections to the students in an understandable way." (Sema)

Another difficulty teacher candidates face about communication is not being able to develop friendly relationships with the students. Two of the teacher candidates expressed that they could not develop friendly relationships with the students. Some of the answers these candidates have given are as follows:

"A general difficulty I encountered while teaching is that I couldn't develop many interactions with students." (Hatice)

"My relationship with the students was very limited because it was the first experience." (Kübra)

Another difficulty teacher candidates face about communication is not being able to use their tone of voice effectively. One of the teacher candidates mentioned not using her tone of voice effectively. The answer given by this candidate is as follows:

"No matter how much I try to control myself, sometimes my voice trembles." (Kübra)

The teacher candidates stated that they did not have difficulties in asking thought-provoking questions appropriate to the subject, carefully listening to the students and effectively using verbal and body language.

Table 1. Difficulties Encountered Regarding Communication

	Sercan	Ahmet	Kübra	Sema	Merve	Betül	Hatice	Sena	Sinem	Ayşe
Being comfortable while teaching	x	x	x	x	x	x	x	x		x
Establishing friendly relationships with students			x				x			
Using the voice of tone effectively			x							
Asking thought-provoking questions appropriate to the topic										
Giving understandable statements and instruction	x			x	x					
Listening to students with the interest										
Using verbal and body language effectively										

3.2. Difficulties Teacher Candidates Face about Classroom Discipline

According to the data in Table 2, the greatest difficulty for candidate teachers about classroom discipline is not being able to manage classroom discipline and control (order, discipline, authority, threat). Six of the teacher candidates mentioned that they could not manage classroom discipline, control and order. Some of the answers these candidates have given are as follows:

"While I am teaching, some of the students try to break the classroom discipline and they don't care even if they are warned." (Sena)

"However, we try to regain the control with the help of our practice teacher." (Ahmet)

"Afterwards, having students that disrupt the order the classroom makes me think that I can't control the class." (Sinem)

Table 2. Difficulties regarding Classroom Discipline

	Sercan	Ahmet	Kübra	Sema	Merve	Betül	Hatice	Sena	Sinem	Ayşe
Classroom discipline and control (order, discipline, authority, threat)		x			x	x		x	x	x

3.3. Difficulties Teacher Candidates Face about Classroom Management

According to the data in Table 3, the greatest difficulty for candidate teachers about classroom management is not being able to attract interest and attention towards the lesson.

Six of the teacher candidates stated that they could not attract students' interest and attention towards the lesson. Some of the answers these candidates have given are as follows:

"We face bloodsucker students in the class. They don't listen, they are not interested. How can I get their attention?" (Betül)

"I sometimes have difficulty in attracting the classroom's attention." (Sema)

Another difficulty teacher candidates face about classroom management is not being able to ensure the continuity of the interest and attention towards the lesson and take appropriate measures against disruptions and obstacles. Five of the teacher candidates stated that they could not ensure the continuity of the interest and attention towards the lesson and take appropriate measures against disruptions and obstacles. Some of the answers these candidates have given are as follows:

"The students who don't care about the lesson make me nervous and they prevent me from teaching effectively." (Ayşe)

"He doesn't want to listen while I teach and he tries to disrupt the class." (Sena)

Another difficulty teacher candidates face about classroom management is about getting back to the subject after a disruption. Three of the teacher candidates mentioned that they could not get back to the subject after a disruption. One of the answers given by these candidates is as follows:

"Even if I know the subject, I get distracted when someone talks and I don't know what to do at that moment." (Merve)

In classroom management, the teacher candidates expressed that they did not have difficulties in making an appropriate introduction to the lesson, using praises and enforcement, creating a democratic learning environment and preparing the students to exit.

Table 3. Difficulties regarding Classroom Management

	Sercan	Ahmet	Kübra	Sema	Merve	Betül	Hatice	Sena	Sinem	Ayşe
Making an appropriate introduction to the lesson										
Attracting interest and attention to the course				x		x	x	x	x	x
Using praise and enforcements										
Giving information and assignments about the next lesson										
Preparing students to exit the classroom										
Providing a democratic learning environment										
Ensuring the continuity of interest and motivation					x	x	x	x		x
Summarizing the lesson					x	x				x
Taking appropriate measures against interruptions and obstacles		x				x		x	x	x

3.4. Difficulties Teacher Candidates Face about Subject Matter

According to the data in Table 4, regarding subject matter, the teacher candidates expressed that they did not have difficulties in regards to basic subject matter principles and concepts, associating the basic subject matter principles and concepts with logical consistency, using verbal and body language (figure, diagram, graph, formula, etc.) required by the subject and associating the subject matter with other subjects.

Table 4. Difficulties regarding Subject Area

	Sercan	Ahmet	Kübra	Sema	Merve	Betül	Hatice	Sena	Sinem	Ayşe
Knowing the basic principles and concepts related to the subject										
Associating to relate basic principles and concepts in the context to logical consistency										
Using verbal and visual language (figure, diagram, graphic, formula etc.)										
Associating the topic with other topics in the field										

3.5. Difficulties Teacher Candidates Face about Subject Matter Education

According to the data in Table 5, the greatest difficulty for candidate teachers about subject matter education is not being able to give appropriate and adequate answers to the questions asked by students. Three of the teacher candidates stated that they could not give appropriate and adequate answers to the questions asked by students. Some of the answers these candidates have given are as follows:

"While I teach, I listen to students' questions and try to I answer the questions in their minds." (Hatice)

"Not to be able to answer when asked a question." (Sena)

The teacher candidates stated that they did not have difficulties about educational approaches, methods and techniques, using instructional technologies, identifying the concepts that were previously learned incorrectly and enduring the security of the learning environment.

Table 5. Difficulties Regarding Subject Matter Education

	Sercan	Ahmet	Kübra	Sema	Merve	Betül	Hatice	Sena	Sinem	Ayşe
Knowing approaches, methods and techniques related to teaching										
Using instructional technologies										
Giving appropriate and adequate answers to student questions				x			x	x		
Identifying students' misdeveloped concepts										
Ensuring the security of the learning environment										

3.6. Difficulties Teacher Candidates Face about the Planning of the Teaching Process

According to the data in Table 6, the greatest difficulty for candidate teachers about the planning of the teaching process is about lesson planning. Two of the teacher candidates mentioned that they could not give appropriate and adequate answers to student questions.
The teacher candidates expressed that they did not have difficulties in writing the lesson plan clearly and organized, stating the goals and desired behaviors clearly, determining methods and techniques appropriate to the desired behaviors and associating the subject with the previous and later lessons.

Table 6. Difficulties Regarding the Planning Teaching Process

	Sercann	Ahmet	Kübra	Sema	Merve	Betül	Hatice	Sena	Sinem	Ayşe
Preparing the lesson plan	x		x							
Writing the lesson plan clearly and regularly										
Stating the goal and target behaviors clearly										
Determining appropriate methods and techniques for target behaviors										
Associating the lesson with the previous and next lessons										

3.7. Difficulties Teacher Candidates Face about the Educational Process

According to the data in Table 7, the greatest difficulty for candidate teachers about the educational process is not being able to use the time effectively. One of the teacher candidates stated that she could not use the time effectively. The teacher candidates expressed that they did not have difficulties in using various teaching methods and techniques appropriately, summarizing and giving appropriate feedbacks, using teaching materials appropriately according to class level, evaluating the achievement level of desired behaviors, organizing activities for effective participation of students and teaching according to individual differences.

Table 7. Difficulties Regarding the Teaching Process

	Sercan	Ahmet	Kübra	Sema	Merve	Betül	Hatice	Sena	Sinem	Ayşe
Using various teaching methods and techniques appropriately										
Summarizing and giving appropriate feedback										
Using instructional equipment and materials appropriate to the class level										
Assessing the level of attainment of target behaviors										
Using time efficiently						x				
Organizing events for active participation of students										
Continuing education according to individual differences										

4. CONCLUSIONS

In this study, the views of teacher candidates who are 4 thy-year students of the faculty of arts and sciences and who are also enrolled in the pedagogical formation certificate program on the difficulties of the Teaching Practice course were determined. The difficulties of the Mathematics teacher candidates were categorized into seven groups: communication, classroom discipline, classroom management, subject area, subject matter education, planning of the teaching process and teaching process.

The greatest difficulty the teacher candidates face about communication is not being able to feel comfortable while teaching. Nine of the candidates stated that they were nervous while teaching because of this. According to Çetintaş and Genç (2005), for teacher candidates to experience a productive process of lesson planning, teaching and evaluation, they need to know the students, individual differences and they need to establish a healthy relationship with the students. For this reason, the practice teacher introducing the teacher candidates to the students during the first class and stating that they have the same authority as himself or herself will also positively affect the attitude of the students towards the candidates. Karadüz et al. (2009) concluded that the qualifications of teacher candidates in communication are developed with the Teaching Practice. Teacher candidates will improve their communication with the students and their own communication skills over time. Therefore, it is believed that mathematics teacher candidates will be able to overcome this difficulty over time. According to Karadüz et al. (2009), in order for the teacher candidates to establish friendly relationships with the students, out-of-class environments should be created for them to interact face-to-face with the students. They should also act by learning the students' level and characteristics. These would contribute to building friendly relationships.

The greatest difficulty for candidate teachers about classroom discipline is not being able to manage classroom discipline and control (order, discipline, authority, threat). Six of the teacher candidates expressed that they could not manage classroom discipline, control and order. Baştürk (2009) stated that half of the teacher candidates had hesitations before teaching such as not being able to control the classroom, being the nervous and quavering voice. Çiçek

and İnce (2005) asked the physical education teacher candidates to write a key word summarizing their expectations from the Teaching Practice course, what they liked and what they did not like about the course, the people whom they got their support from and what they experienced every week, and why they chose this Word keyword using a couple of sentences. In Çiçek and İnce's (2005) study, students stated classroom discipline and control, and classroom management is the things they liked the least by the end of the course. According to Baştürk (2009), before teaching half of the teacher candidates had hesitations like not being able to control the classroom, being the nervous and quavering voice. These difficulties were reduced by the end of the term. It is stated that inexperienced teachers who have just started their profession have difficulties in class management and discipline during their first years. It can be said that the support given by the practice teachers to the candidates is important.

The greatest difficulty for candidate teachers about classroom management is not being able to attract students' interest and attention towards the lesson. Six of the teacher candidates stated that they could not attract students' interest and attention towards the lesson. Not being able to take appropriate measures against disruptions and obstacles (five students) and not being able to ensure the continuity of students' interest and attention towards the lesson (five students) are the other difficulties mathematics teacher candidates face regarding classroom management. The teacher candidates stated that they did not have difficulties in making an appropriate introduction to the lesson, using praises and enforcement, creating a democratic learning environment and preparing the students to exit. The difficulties that candidate teachers face in regards to classroom management are actually related to competencies that are not sufficiently developed during Teaching Practice. According to Karadüz et al. (2009), who reached the conclusion that Teaching Practice did not improve the classroom management competencies of the teacher candidates, practice teachers' desire to class control in their own hands, sudden interventions during the class and not trusting the teacher candidate cause this situation. Karadüz et al. (2009) argue that the teacher candidates to be given enough incentives and the guidance teachers should not be too intrusive by providing external control. Therefore, these difficulties faced by the teacher candidates will continue until cooperation between the teacher candidate and the practice teacher developed.

In regards to subject matter, the teacher candidates stated that they did not have any difficulties. The results show that teacher candidates did not have difficulties in knowing basic subject matter principles and concepts, associating the basic subject matter principles and concepts with logical consistency, using verbal and body language (figure, diagram, graph, formula, etc.) required by the subject and associating the subject matter with other subjects. This shows that candidates' theoretical knowledge is complete. Other than subject matter, teacher candidates are struggling in the communication, classroom discipline, classroom management, subject matter education, planning of the teaching process and educational process.

Regarding subject matter education, the greatest difficulty for candidate teachers is not being able to give appropriate and adequate answers to student questions. Three of the teacher candidates mentioned that they could not give appropriate and adequate answers to student questions. The candidates stated that they did not have difficulties with educational approaches, methods and techniques, using instructional technologies, identifying the concepts that were previously learned incorrectly and enduring the security of the learning environment. In their study, Akpınar et al. (2012) found that the social studies teacher candidates described themselves as both competent and incompetent in the selection and use of methods and techniques. This incompetency was attributed to the students' attitudes such as anxiety about not being appointed because of KPSS, inexperience, coming unprepared to class and indifference. Akpınar et al. (2012) also stated that social science teacher candidates

could not use modern teaching methods such as drama and cooperative learning. The reason for this is their worry about losing classroom control and the easiness of using traditional methods. Even though they seem to be reluctant from time to time, teacher candidates were found to use instructional technologies such as projection and to prepare and use materials, especially worksheets, in accordance with the curriculum, objectives and student level (Akpınar, Çolak & Yiğit, 2012). Therefore, mathematics teacher candidates not having difficulty in using different methods can be attributed to the courses they have taken during pedagogical formation program. Their ease of using instructional technologies can be attributed to their technology education both during and before their undergraduate education.

In regards to planning of the teaching process, the greatest difficulty for candidate teachers is about lesson planning. Two of the teacher candidates stated that they could not give appropriate and adequate answers to student questions. The teacher candidates expressed that they did not have difficulties in writing the lesson plan clearly and organized, stating the goals and desired behaviors clearly, determining methods and techniques appropriate to the desired behaviors and associating the subject with the previous and later lessons. Teacher candidates' difficulties regarding the planning of the teaching process can be determined and eliminated by giving them the opportunity to practice more during the Special Teaching Methods course before they start their Teaching Practice (Akpınar, Çolak & Yiğit, 2012). To be able to eliminate the difficulty of "not giving appropriate and adequate answers to student questions", students should be able to practice the question-answer method more during the Special Teaching Methods course.

Regarding the educational process, the greatest difficulty for candidate teachers is not being able to use the time effectively. One of the teacher candidates mentioned that she could not use the time effectively. On the other hand, the teacher candidates stated that they did not have difficulties in areas such as using various teaching methods and techniques appropriately, summarizing and giving appropriate feedbacks, using teaching materials, evaluation, ensuring student participation and individual differences. The main reason why teacher candidates have difficulties in some areas is that they only have six hours a week in the practice school. This is mentioned by both of the teacher candidates' practice teachers who are working in the Niğde high schools where the teacher candidates went to fro practice. When the hours of practice are limited to only six hours, the teacher candidates graduate without experiencing different aspects of the school atmosphere, such as classroom management, material use, practicing different teaching methods, evaluation, and cooperating with the school. (Akpınar et al., 2012). Increasing the number of practice hours and candidates attending to various activities (such as subject group meetings, administrative matters) at the practice school will make the Teaching Practice course more efficient (Akpınar, Çolak & Yiğit, 2012).

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On the Commutativity of a Prime $*$-Ring with a $*$-α-Derivation[1]

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Abstract: *Let R be a prime $*$-ring where $*$ be an involution of R, α be an automorphism of R, T be a nonzero left α-$*$-centralizer on R and d be a nonzero $*$-α-derivation on R. The aim of this paper is to prove the commutativity of a $*$-ring R with the followings conditions: i) if T is a homomorphism (or an anti-homomorphism) on R,ii) if $d([x,y])=0$ for all $x,y\in R$, iii) if $[d(x),y]=[\alpha(x),y]$ for all $x,y\in R$, iv) if $d(x)\circ y=0$ for all $x,y\in R$, v) if $d(x\circ y)=0$ for all $x,y\in R$.*

Keywords: *$*$-derivation, $*$-α-derivation, left $*$-centralizer, left α-$*$-centralizer.*
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1. Introduction

Let R be a ring and $Z(R)$ be the center of R. $x,y\in R$ such that $xy-yx$, $xy+yx$ are denoted by $[x,y]$ and $x\circ y$ respectively and the followings are hold for all $x,y\in R$

- $[x,yz]=[x,y]z+y[x,z]$
- $[xy,z]=[x,z]y+x[y,z]$

[1]This study is the revised version of the paper (A Note On $*$-α-Derivations of Prime *-Rings) presented in the "2nd International Rating Academy Congress: Hope" held in Kepez / Çanakkale on April 19-21, 2018

- $(xy) \circ z = x(y \circ z) - [x, z]y = (x \circ z)y + x[y, z]$
- $x \circ (yz) = (x \circ y)z - y[x, z] = y(x \circ z) + [x, y]z$.

R is called a *prime* (*resp.* semiprime) *ring* if $a, b \in R$ such that $aRb = (0)$ then either $a = 0$ or $b = 0$ (*resp.* If $aRa = (0)$ then $a = 0$). $* : R \to R$ is an additive mapping such that $(xy)^* = y^*x^*$ and $(x^*)^* = x$ is called an *involution* and a ring equipped with an involution is called a $*$-*ring*. If a $*$-ring is prime (*resp.* semiprime) then it is called a *prime* (*resp.* semiprime) $*$-*ring*.

An additive mapping d of R is called a *derivation* if $d(xy) = d(x)y + xd(y)$ for all $x, y \in R$. The authors have been trying to decide that whether a ring is commutative or not with the help of derivation that is defined over the ring. First study was made on this subject by Posner in [4]. Bresar and Vukman in [5] defined a $*$-*derivation* on a $*$-ring as follows: an additive mapping d of R is called a derivation if $d(xy) = d(x)y^* + xd(y)$ for all $x, y \in R$. Kim and Lee showed that in [2] the ring is commutative using some identities with a $*$-derivation which is defined on a prime $*$-ring and semiprime $*$-ring where $*$ is an involution. Firstly, inspired by the definition of $*$-derivation, it is given that d is a $*$-α-*derivation* if $d(xy) = d(x)y^* + \alpha(x)d(y)$ for all $x, y \in R$ where α is a homomorphism on R. Same results are obtained using similar hypothesis in Kim and Lee's paper with $*$-α-derivation which is defined on a prime $*$-ring and semiprime $*$-ring in this study.

In 1957, the *reverse derivation* is defined by Herstein in [6] as follows: the reverse derivation is an additive mapping d of R such that $d(xy) = d(y)x + yd(x)$ for all $x, y \in R$. After this definition, Breaser and Vukman defined the reverse $*$-derivation in [5] as follows: the reverse $*$-derivation is an additive mapping d of R such that $d(xy) = d(y)x^* + yd(x)$ for all $x, y \in R$. Inspired by the definition of reverse $*$-derivation, it is given that d is called a *reverse* $*$-α-*derivation* if $d(xy) = d(y)x^* + \alpha(y)d(x)$ for all $x, y \in R$ where $\alpha : R \longrightarrow R$ is a homomorphism. Kim and Lee showed in [2] that if d is a reverse $*$-derivation of semiprime $*$-ring then it holds $[d(x), z] = 0$ for all $x, z \in R$. This result is given for reverse $*$-α-derivation in this study.

Zalar defined in [7] the *left centralizer* (*etc.* right centralizer) as follows: the left centralizer is an additive mapping T on R such that $T(xy) = T(x)y$ for all $x, y \in R$. Ali and Fosner in [8] defined the left $*$-centralizer on a $*$-ring where $*$ is an involution as follows: a left $*$-centralizer (*etc.* right $*$-centralizer) is an additive mapping T such that $T(xy) = T(x)y^*$ for all $x, y \in R$. In [9], Koç and Gölbaşı said to a *left* α-$*$-*centralizer* (*etc.* right α-$*$-centralizer) that T is an additive mapping

such that $T(xy) = T(x)\alpha(y^*)$ for all $x, y \in R$ where α is a homomorphism. Kim et al. proved that in [2] if R is a semiprime $*$-ring and $T : R \to R$ is a left $*$-centralizer then $T : R \to Z(R)$. Rehman et al showed that in [3] if R is a 2-torsion free semiprime $*$-ring and T is both a Jordan $*$-centralizer and a homomorphism on R then $T : R \to Z(R)$. Furthermore, if R is a 2-torsion free prime $*$-ring and T is a nonzero Jordan $*$-centralizer then $T = *$. In the following part of this study, based upon the results are proved by Kim and Lee in [2] and Rehman et al.in [3], if a left α-$*$-centralizer defined over a prime $*$-ring where α is an automorphism, is also a homomorphism (or an anti-homomorphism), then the ring is commutative.

Throughout this paper, R is a prime or semiprime $*$-ring where $*$ is an involution, $\alpha : R \to R$ is an automorphism, d is a nonzero $*$-α-derivation of R and T is a left α-$*$-centralizer on R.

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2. Results

Lemma 2.1. *[1,Lemma 1.1.4] Suppose that R is semi-prime and that $a \in R$ is such that $a(ax - xa) = 0$ for all $x \in R$. Then $a \in Z(R)$, the center of R.*

Theorem 2.2. *Let R be a $*$-ring where $* : R \to R$ be an involution, α be an automorphism of R and T be a nonzero left α-$*$-centralizer on R.*

i) *If R is semiprime then the mapping T is R into $Z(R)$.*
ii) *If R is prime and T is a homomorphism (or an anti-homomorphism) on R, then R is commutative.*

Proof. i) Let R be semiprime. If it is observed $T(xz^*y^*)$ for $x, y, z \in R$, it is obtained respectively for all $x, y, z \in R$

$$T(xz^*y^*) = T(x(z^*y^*)) = T(x)\alpha((z^*y^*)^*) = T(x)\alpha(yz) = T(x)\alpha(y)\alpha(z) \tag{1}$$

and

$$T(xz^*y^*) = T((xz^*)y^*) = T(xz^*)\alpha((y^*)^*) = T(x)\alpha((z^*)^*)\alpha(y) = T(x)\alpha(z)\alpha(y) \tag{2}$$

Combining the equation (1) and (2), it holds that

$$T(x)[\alpha(y), \alpha(z)] = 0 \text{ for all } x, y, z \in R.$$

Since α is onto mapping, replacing $\alpha(y)$ by $T(x)$ in last equation, it holds

$$T(x)[T(x), \alpha(z)] = 0 \text{ for all } x, y, z \in R.$$

Since α is onto mapping, this means that

$$T(x)[T(x), z] = 0 \text{ for all } x, y, z \in R.$$

From Lemma 2.1, it gets $T(x) \in Z(R)$ for all $x \in R$ which means that $T : R \to Z(R)$.

ii) Let R be prime and T be a homomorphism of R. Since T is a homomorphism, it holds

$$T(xy) = T(x)T(y) \text{ for all } x, y \in R. \tag{3}$$

Also, since T is a left α-$*$-centralizer, it has

$$T(xy) = T(x)\alpha(y^*) \text{ for all } x, y \in R. \tag{4}$$

Combining equations (3) and (4) it holds

$$T(x)T(y) = T(x)\alpha(y^*) \text{ for all } x, y \in \ R. \tag{5}$$

Replacing y by y^*z^* where $z \in R$ in equation (5), it is obtained

$$T(x)T(y^*)\alpha(z) = T(x)\alpha(z)\alpha(y) \text{ for all } x, y, z \in R.$$

By using (5) it gets

$$T(x)\alpha(y)\alpha(z) = T(x)\alpha(z)\alpha(y) \text{ for all } x, y, z \in R.$$

And so,

$$T(x)[\alpha(z), \alpha(y)] = 0 \text{ for all } x, y, z \in R$$

is obtained. In the last equation, replacing x by xs^* where $s \in R$ and using that α is an onto mapping, it gets

$$T(x)R[\alpha(z), \alpha(y)] = (0) \text{ for all } x, y, z \in R.$$

Since R is a prime $*$-ring, it implies either $T = 0$ or $[\alpha(z), \alpha(y)] = 0$ for all $y, z \in R$. Since T is nonzero, it implies that R is commutative.

Now let R be prime and T be an anti-homomorphism of R. Since T is an anti-homomorphism, it gets

$$T(xy) = T(y)T(x) \text{ for all } x, y \in R. \tag{6}$$

Moreover, since T is a left α-$*$-centralizer, it has

$$T(xy) = T(x)\alpha(y^*) \text{ for all } x, y \in R. \tag{7}$$

If the equations (6) and (7) are considered together and edited, it follows

$$T(y)T(x) = T(x)\alpha(y^*) \text{ for all } x, y \in R. \tag{8}$$

Replacing x by zx^* and y by y^* where $z \in R$ in the last equation, it holds

$$T(y^*)T(zx^*) = T(zx^*)\alpha((y^*)^*) \text{ for all } x, y, z \in R.$$

The last equation is edited by using the equation (8) , it follows

$$T(z)[\alpha(x), \alpha(y)] = 0 \text{ for all } x, y, z \in R.$$

Replacing z by zt^* where $t \in R$ in the last equation and using α is an onto mapping it gets

$$T(z)R[\alpha(x), \alpha(y)] = (0) \text{ for all } x, y, z \in R.$$

Since R is a prime $*$-ring, it implies that either $T = 0$ or $[\alpha(x), \alpha(y)] = 0$ for all $x, y \in R$. Since α is an onto mapping and T is a nonzero mapping, it gets that R is commutative. □

Theorem 2.3. *Let R be a $*$-ring where $* : R \to R$ be an involution, α be an automorphism of R and d be a nonzero $*$-α-derivation on R.*

i) *If R is semiprime, then d is R into $Z(R)$.*
ii) *If R is prime and d acts as a homomorphism on R, then $d = \alpha$.*
iii) *If R is prime and d acts as an anti-homomorphism, then $d = *$.*

Proof.

i) Let R be semiprime. If it is observed $d(xy^*z^*)$ for $x, y, z \in R$ by using that d is a nonzero $*$-α-derivation, it is obtained

$$d(xy^*z^*) = d(x(y^*z^*)) = d(x)zy + \alpha(x)d(y^*)z + \alpha(xy^*)d(z^*) \tag{9}$$

and

$$d(xy^*z^*) = d((xy^*)z^*) = d(x)yz + \alpha(x)d(y^*)z + \alpha(xy^*)d(z^*). \tag{10}$$

Combining the equations (9) and (10), it implies

$$d(x)[z, y] = 0 \text{ for all } x, y, z \in R.$$

Replacing z by $d(x)$ in last equation, by using the Lemma 2.1 the desired result is obtained.

ii) Let R be prime and d be a homomorphism. Since d is both a homomorphism and a $*$-α-derivation, it holds

$$d(xy) = d(x)y^* + \alpha(x)d(y) = d(x)d(y) \text{ for all } x, y \in R.$$

Replacing x by xz where $z \in R$ in the last equation and by using that d is a homomorphism, it implies for all $x, y, z \in R$

$$d(x)d(z)y^* + \alpha(x)\alpha(z)d(y) = d(x)d(z)d(y) = d(x)d(zy)$$

is obtained.

$$d(x)d(z)y^* + \alpha(x)\alpha(z)d(y) = d(x)d(z)y^* + d(x)\alpha(z)d(y) \text{ for all } x, y, z \in R.$$

Since α is onto mapping, it follows

$$(\alpha(x) - d(x))Rd(y) = (0) \text{ for all } x, y \in R.$$

Since R is a prime $*$-ring and d is a nonzero mapping, it is obtained that $d = \alpha$.

iii) Let R be prime and d be an anti-homomorphism. Since d is both an anti-homomorphism and a $*$-α-derivation,

$$d(xy) = d(x)y^* + \alpha(x)d(y) = d(y)d(x).$$

Replacing y by xy^* in last equation and by using that d is an anti-homomorphism, it follows

$$d(x)yx^* + \alpha(x)d(y^*)d(x) = d(x)yd(x) + \alpha(x)d(y^*)d(x).$$

So, it implies

$$d(x)R(d(x) - x^*) = (0) \text{ for all } x \in R.$$

Since R is prime $*$-ring, it implies that either $d(x) = x^*$ or $d(x) = 0$. We set that $A = \{x \in R \mid d(x) = x^*\}$ and $B = \{x \in R \mid d(x) = 0\}$. Then A and B are both additive subgroups of R and R is the union A and B but a group can not be set union of its two proper subgroups. Hence, R equals that either A or B. Assume that $B = R$ which means that $d = 0$ which is a contradiction. So it follows that $A = R$ which means that $d = *$. □

Theorem 2.4. *Let R be a prime $*$-ring where $* : R \to R$ be an involution, α be an automorphism of R and d be a nonzero $*$-α-derivation on R. If $d([x, y]) = 0$ for all $x, y \in R$, then R is commutative.*

Proof. Replacing x by xy in the hypothesis and by using that d is a $*$-α-derivation, it holds

$$\alpha([x,y])d(y) = 0 \text{ for all } x, y \in R.$$

Replacing x by xs where $s \in R$ in last equation and using that α is an onto mapping, it hold

$$\alpha([x,y])Rd(y) = (0) \text{ for all } x, y \in R.$$

Since R is a prime $*$-ring, it implies that either $\alpha([x,y]) = 0$ or $d(y) = 0$ for all $x, y \in R$. Since d is nonzero and α is onto, it follows that R is commutative by using the similar method in the proof of (iii) of Theorem 2.3. □

Theorem 2.5. *Let R be a prime $*$-ring where $* : R \to R$ be an involution, $\alpha : R \to R$ be an automorphism and $d : R \to R$ be a nonzero $*$-α-derivation. If $[d(x), y] = [\alpha(x), y]$ for all $x, y \in R$, then R is commutative.*

Proof. Replacing x by xz where $z \in R$ and by using that d is a $*$-α-derivation, it holds

$$[d(x)z^*, y] + [\alpha(x)d(z), y] = \alpha(x)[\alpha(z), y] + [\alpha(x), y]\alpha(z) \text{ for all } x, y, z \in R. \tag{11}$$

Replacing y by $\alpha(x)$ in hypothesis, it holds

$$[d(x), \alpha(x)] = 0.$$

Furthermore, replacing y by $\alpha(x)$ in (11) and by using that $[d(x), \alpha(x)] = 0$, it implies

$$d(x)[z^*, \alpha(x)] = 0 \text{ for all } x, z \in R.$$

Replacing z by $(zr)^*$ where $r \in R$ and by using the last equation, it holds

$$d(x)R[r, \alpha(x)] = (0) \text{ for all } x, r \in R.$$

Since R is prime $*$-ring, it implies that either $d(x) = 0$ or $[r, \alpha(x)] = 0$ for all $x, r \in R$. Since d is nonzero and α is onto, it follows that R is commutative by using the similar method in the proof of (iii) of Theorem 2.3. □

Theorem 2.6. *Let R be a prime $*$-ring where $* : R \to R$ be an involution, α be an automorphism and d be a nonzero $*$-α-derivation on R. If $a \in R$ such that $[d(x), \alpha(a)] = 0$ for all $x \in R$ then $d(a) = 0$ or $a \in Z(R)$.*

Proof. Replacing for x by xy where $y \in R$ in the hypothesis and by using that d is a $*$-α-derivation, it implies

$$d(x)[y^*, \alpha(a)] + [\alpha(x), \alpha(a)]d(y) = 0 \text{ for all } x, y \in R.$$

Replacing x by a in the last equation

$$d(a)[y^*, \alpha(a)] = 0 \text{ for all } y \in R.$$

Replacing y by $(yr)^*$where $r \in R$ in the last equation, it implies

$$d(a)R[r, \alpha(a)] = (0) \text{ for all } r \in R.$$

Since R is a prime $*$- ring and α is an onto mapping, it follows that either $d(a) = 0$ or $a \in Z(R)$. □

Theorem 2.7. *Let R be a semiprime $*$-ring where $* : R \to R$ be an involution and α be an automorphism of R. If d is a nonzero reverse $*$-α-derivation on R, the mapping d is R into $Z(R)$.*

Proof. Since d is a reverse $*$-α-derivation, it holds

$$d(xy) = d(y)x^* + \alpha(y)d(x) \text{ for all } x, y \in R.$$

Replacing x by xz and y by zy where $z \in R$ in the last equation respectively, it gets that for all $x, y, z \in R$

$$d((xz)y) = d(y)z^*x^* + \alpha(y)d(z)x^* + \alpha(y)\alpha(z)d(x). \tag{12}$$

and

$$d(x(zy)) = d(y)z^*x^* + \alpha(y)d(z)x^* + \alpha(z)\alpha(y)d(x). \tag{13}$$

Combining equations (12) and (13), it implies

$$[\alpha(y), \alpha(z)]d(x) = 0 \text{ for all } x, y, z \in R. \tag{14}$$

Replacing y by yr where $r \in R$ in the last equation, it holds

$$[\alpha(y), \alpha(z)]\alpha(r)d(x) = 0 \text{ for all } x, y, z, r \in R. \tag{15}$$

On the other hand, the equation (14) multiplies by $\alpha(r)$ from right side, it holds

$$[\alpha(y), \alpha(z)]d(x)\alpha(r) = 0 \text{ for all } x, y, z, r \in R. \tag{16}$$

Combining equations(15) and (16), it implies

$$[\alpha(y), \alpha(z)][\alpha(r), d(x)] = 0 \text{ for all } x, y, z, r \in R.$$

Since α is onto, it holds

$$[y, z][r, d(x)] = 0 \text{ for all } x, y, z, r \in R. \tag{17}$$

Replacing y by r and z by $d(x)s$ where $s \in R$ in the last equation and by using the equation (17), it follows

$$[r, d(x)]R[r, d(x)] = (0) \text{ for all } r, x \in R.$$

Since R is a semiprime $*$-ring, d is R into $Z(R)$ which means that $d : R \to Z(R)$. □

Theorem 2.8. *Let R be a prime $*$-ring where $* : R \to R$ be an involution, α be an automorphism and d be a nonzero $*$-α-derivation on R. If $d(x) \circ y = 0$ for all $x, y \in R$, then R is commutative.*

Proof. Replacing x by xz where $z \in R$ in the hypothesis, it holds

$$d(x)[z^*, y] - [\alpha(x), y]d(z) = 0 \text{ for all } x, y, z \in R.$$

Replacing y by $\alpha(x)$ in last equation,

$$d(x)[z^*, \alpha(x)] = 0 \text{ for all } x, y \in R$$

is obtained. Replacing z by $(rz)^*$ where $r \in R$ in the last equation and by using α is an onto mapping with the last equation, it gets

$$d(x)R[z, \alpha(x)] = (0) \text{ for all } x, z \in R.$$

Since R is a prime $*$-ring, it follows that either $d(x) = 0$ or $[z, \alpha(x)] = 0$ for all $z, x \in R$. Since d is nonzero and α is onto, it follows that R is commutative by using the similar method in the proof of (iii) of Theorem 2.3. □

Theorem 2.9. *Let R be a prime $*$-ring, where $* : R \to R$ be an involution, α be an automorphism and d be a nonzero $*$-α-derivation on R. If $d(x \circ y) = 0$ for all $x, y \in R$, then R is commutative.*

Proof. Replacing x by xy in hypothesis, it holds

$$d((x \circ y)y) = \alpha(x \circ y)d(y) = 0 \text{ for all } x, y \in R.$$

Furthermore replacing x by xz where $z \in R$ in the last equation and by using that α is an onto mapping

$$\alpha([x,y])Rd(y) = (0) \text{ for all } x, y \in R$$

is obtained. Since R is a prime $*$-ring, it implies that either $\alpha([x,y]) = 0$ or $d(y) = 0$ for all $x, y \in R$. Since d is nonzero and α is onto, it follows that R is commutative by using the similar method in the proof of (iii) of Theorem 2.3. □

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Generalized Reverse Derivations On Closed Lie Ideals[1]

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Abstract: *In this study, we investigate commutavity of prime ring R with generalized reverse derivations F and G. Also, we proved that if L is a square closed Lie ideal, then L is contained in center Z (R) under given conditions in theorems.*

Keywords: *Prime ring, Lie ideal, Reverse derivation, Generalized reverse derivation.*
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1. Introduction

Let R be a ring with center $Z(R)$. Recall that R is prime if for any $x, y \in R$, $xRy = (0)$ implies $x = 0$ or $y = 0$. An additive mapping d form R into R is called derivation if $d(xy) = d(x)y + xd(y)$ for all $x, y \in R$. In [3], Bresar generalized concept of derivation as the following: An additive mapping F from R into R is called generalized derivation with associated derivation d if $F(xy) = F(x)y + xd(y)$ for all $x, y \in R$. In [4], Bresar and Vukman introduced reverse derivation and in [1],

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Abuabakar and Gonzalez introduced generalized reverse derivation. Let d from R into R be an additive mapping. If $d(xy) = d(y)x + yd(x)$ holds for all $x, y \in R$, then d is called right reverse derivation. Let F from R into R be an additive mapping. If $F(xy) = d(y)x + yF(x)$ holds for all $x, y \in R$, then F is called right generalized reverse derivation with associated reverse derivation d.

For any $x, y \in R$ denote the notation $[x, y]$ for commutator $xy - yx$ and $x \circ y$ for anti-commutator $xy + yx$. We use the following basic identities.

- $[xy, z] = x[y, z] + [x, z]y$
- $[x, yz] = [x, y]z + y[x, z]$
- $(xy) \circ z = x(yoz) - [x, z]y = (x \circ z)y + x[y, z]$
- $x \circ (yz) = (x \circ y)z - y[x, z] = y(x \circ z) + [x, y]z$

Let L be an additive subgroup of R. L is said to be a Lie ideal of R if $[L, R] \subseteq R$. A Lie ideal L is said to be a square closed Lie ideal if $x^2 \in L$ for all $x \in L$.

In [5], Posner showed that two important properties of prime rings with derivation. In a prime ring R with $charR \neq 2$, if the iterate of two derivations is a derivation, then one of them is zero, and if d is a derivation and $[a, d(a)] \in Z(R)$ for all $a \in R$, then either R is commutative or d is zero. After that, several authors have proved commutativity theorems for prime rings with derivation and generalized derivation. Also many researchers have generalized results to ideals and Lie ideals of ring. In [2], Al-Omary and Rehman showed that if L is a square closed Lie ideal of prime ring with generalized derivation, then $L \subseteq Z(R)$ under several conditions.

In this study, we generalize previous studies on prime rings with reverse derivation. Let R be a prime ring with $charR \neq 2$, $F : R \to R$ be a nonzero right generalized reverse derivation with associated right reverse derivation $d : R \to R$ and L be a nonzero square closed Lie ideal of R such that $d(Z(L)) \neq (0)$. We study following conditions and prove $L \subseteq Z(R)$. (i) $[F(x), x] \in Z(R)$ for all $x \in L$. (ii) $F(x) \circ x \in Z(R)$ for all $x \in L$. (iii) $F(x \circ y) - [x, y] \in Z(R)$ for all $x, y \in L$. (iv) $F[x, y] - x \circ y \in Z(R)$ for all $x, y \in L$. (v) $[F(x), d(y)] - [x, y] \in Z(R)$ for all $x, y \in L$. (vi) $[F(x), F(y)] - [x, y] \in Z(R)$ for all $x, y \in L$. (vii) $F(x) \circ F(y) - x \circ y \in Z(R)$ for all $x, y \in L$. $(viii)$ $[F(x), F(y)] - x \circ y \in Z(R)$ for all $x, y \in L$. (ix) $F(x) \circ F(y) - [x, y] \in Z(R)$ for all $x, y \in L$. (x) $[F(x), F(y)] - F[x, y] \in Z(R)$ for all $x, y \in L$. (xi) $F(x) \circ F(y) - F(x \circ y) \in Z(R)$ for all $x, y \in L$. (xii) $F[x, y] - [F(x), y] \in Z(R)$ for all $x, y \in L$. $(xiii)$ $F[x, y] + [F(x), y] - [F(x), F(y)] \in Z(R)$ for all $x, y \in L$. (xiv) $F[x, y] - F(x) \circ y - [d(y), x] \in Z(R)$ for all $x, y \in L$.

In addition, we investigate commutative property for two nonzero right generalized reverse derivations $F, G : R \to R$ with associated right reverse derivations $d, g : R \to R$ respectively. We study following conditions and prove $L \subseteq Z(R)$. (i) $[F(x), G(y)] - [x, y] \in Z(R)$ for all $x, y \in L$. (ii) $[F(x), x] - [x, G(x)] \in Z(R)$ for all $x, y \in L$. (iii) $F(x) \circ x - x \circ G(x) \in Z(R)$ for all $x, y \in L$. (iv) $F[x, y] - [y, G(x)] \in Z(R)$ for all $x, y \in L$. (v) $F(x \circ y) - y \circ G(x) \in Z(R)$ for all $x, y \in L$.

2. Preliminaries

Well-known fact about prime rings:

Remark 2.1. *Let R be a prime ring. For an elements $a \in Z(R)$ and $b \in R$, if $ab \in Z(R)$, then $b \in Z(R)$ or $a = 0$.*

Remark 2.2. *Let R be a prime ring with $charR \neq 2$ and L be a square closed Lie ideal of R. Then $2ab \in L$ for all $a, b \in L$.*

Lemma 2.3. [6, Lemma 2.6] *Let R be a $2-$torsion free semiprime ring and L be a nonzero Lie ideal of R. If L is a commutative Lie ideal of R, i. e., $[x, y] = 0$ for all $x, y \in L$, then $L \subseteq Z(R)$.*

Lemma 2.4. [7, Lemma 2.5] *Let R be a $2-$torsion free semiprime ring and L be a nonzero Lie ideal of R. Then $Z(L) \subseteq Z(R)$.*

3. Results

Lemma 3.1. *Let R be a prime ring with $char(R) \neq 2$ and L be a nonzero square closed Lie ideal of R. If $[x, y] \in Z(R)$ for all $x, y \in L$, then $L \subseteq Z(R)$.*

Proof. Let $[x, y] \in Z(R)$ for all $x, y \in L$. Then $[r, [x, y]] = 0$ for all $x, y \in L$, $r \in R$. Replacing x by $2xy$, we get $0 = [r, [2xy, y]] = 2[r, [xy, y]]$ and using $char(R) \neq 2$, we have $[x, y][r, y] = 0$. Replacing r by rs for any $s \in R$, we find $[x, y] r [s, y] = 0$ for all $x, y \in L$, $r, s \in R$. Since R is a prime ring, we obtain

$$[x, y] = 0 \text{ or } [s, y] = 0 \text{ for all } x, y \in L, s \in R.$$

If $[s, y] = 0$, then $y \in Z(R)$ and satisfy condition $[x, y] = 0$. So, $[x, y] = 0$ for all $x, y \in L$ in both cases. From the Lemma 2.3 we get $L \subseteq Z(R)$. □

Lemma 3.2. *Let R be a prime ring with $char(R) \neq 2$ and L be a nonzero square closed Lie ideal of R. If $x \circ y \in Z(R)$ for all $x, y \in L$, then $L \subseteq Z(R)$.*

Proof. Let $x \circ y \in Z(R)$ for all $x, y \in L$. Then $[r, x \circ y] = 0$ for all $x, y \in L$, $r \in R$. Replacing x by $2xy$, we get $0 = [r, 2xy \circ y] = 2[r, xy \circ y]$ and using $char(R) \neq 2$, we have $(x \circ y)[r, y] = 0$. Replacing r by rs for any $s \in R$, we find $(x \circ y) r [s, y] = 0$ for all $x, y \in L$, $r, s \in R$. Since R is a prime ring, we obtain

$$x \circ y = 0 \text{ or } [s, y] = 0 \text{ for all } x, y \in L, \ s \in R.$$

Let $A = \{y \in L \mid x \circ y = 0 \text{ for all } x \in L\}$ and $B = \{y \in L \mid [s, y] = 0 \text{ for all } s \in R\}$. A and B are additive subgroups of L whose $L = A \cup B$, but a group can not be written as a union of two proper subgroups of its and hence $L = A$ or $L = B$. If $L = A$, then $x \circ y = 0$ for all $x \in L$. Replacing y by $2yz$ for any $z \in L$ and using $char(R) \neq 2$, we get $[x, y] z = 0$ for all $x, y, z \in L$. In this equation, replacing z by $[z, r]$ for any $r \in R$ we find $[x, y][z, r] = 0$ for all $x, y, z \in L$, $r \in R$. Again replacing r by rs for any $s \in R$, we get $[x, y] r [z, s] = 0$ for all $x, y, z \in L$, $r, s \in R$. Since R is a prime ring, we obtain

$$[x, y] = 0 \text{ or } [z, s] = 0 \text{ for all } x, y, z \in L, s \in R.$$

If $[x, y] = 0$, then from the Lemma 2.3 we get $L \subseteq Z(R)$. If $[z, s] = 0$, then $z \in Z(R)$ for all $z \in L$ and $L \subseteq Z(R)$. If $L = B$, then $[s, y] = 0$ for all $s \in R$, $y \in L$. Hence, we obtain $y \in Z(R)$ for all $y \in L$ and $L \subseteq Z(R)$. □

Lemma 3.3. *Let R be a prime ring with $char(R) \neq 2$, $0 \neq F : R \longrightarrow R$ be a right generalized reverse derivation with associated right reverse derivation d and L be a nonzero square closed Lie ideal of R such that $d(Z(L)) \neq (0)$. If $[F(x), x] \in Z(R)$ for all $x, y, z \in L$, then $L \subseteq Z(R)$.*

Proof. Let $[F(x), x] \in Z(R)$ for all $x, y, z \in L$. Replacing x by $x + y$, we get

$$[F(x), y] + [F(y), x] \in Z(R) \text{ for all } x, y \in L \tag{1}$$

Since $d(Z(L)) \neq (0)$, we choose fixed element $0 \neq z \in Z(L)$ which $d(z) \neq 0$. Also, $z, d(z) \in Z(R)$ from the Lemma 2.4. Replacing x by $2xz$ in Equation (1) and using $char(R) \neq 2$, we get

$$d(z)[x, y] + [d(z), y] x + z[F(x), y] + [z, y] F(x) + [F(y), x] z + x[F(y), z] \in Z(R)$$

In this expression, using $z, d(z) \in Z(R)$ and Equation (1), we have

$$d(z)[x, y] \in Z(R) \text{ for all } x, y \in L$$

Hence, using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we obtain $[x, y] \in Z(R)$ for all $x, y \in L$. From the Lemma 3.1 we get $L \subseteq Z(R)$. □

Lemma 3.4. *Let R be a prime ring with $char(R) \neq 2$, $0 \neq F : R \longrightarrow R$ be a right generalized reverse derivation with associated right reverse derivation d and L be a nonzero square closed Lie ideal of R such that $d(Z(L)) \neq (0)$. If $F(x) \circ x \in Z(R)$ for all $x, y, z \in L$, then $L \subseteq Z(R)$.*

Proof. Let $F(x) \circ x \in Z(R)$ for all $x, y, z \in L$. Replacing x by $x + y$, we get

$$F(x) \circ y + F(y) \circ x \in Z(R) \text{ for all } x, y \in L \tag{2}$$

Since $d(Z(L)) \neq (0)$, we choose fixed element $0 \neq z \in Z(L)$ which $d(z) \neq 0$. Also, $z, d(z) \in Z(R)$ from the Lemma 2.4. Replacing x by $2xz$ in Equation (2) and using $char(R) \neq 2$, we get

$$(d(z)x) \circ y + (zF(x)) \circ y + F(y) \circ (xz) \in Z(R) \text{ for all } x, y \in L$$

In this expression, using $z, d(z) \in Z(R)$ and Equation (2), we have

$$d(z)(x \circ y) \in Z(R) \text{ for all } x, y \in L$$

Hence, using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we obtain $x \circ y \in Z(R)$ for all $x, y \in L$. From the Lemma 3.2 we get $L \subseteq Z(R)$. □

Theorem 3.5. *Let R be a prime ring with $char(R) \neq 2$, $0 \neq F : R \longrightarrow R$ be a right generalized reverse derivation with associated right reverse derivation d and L be a nonzero square closed Lie ideal of R such that $d(Z(L)) \neq (0)$. If one of the following conditions is satisfy, then $L \subseteq Z(R)$.*

i) $F(x \circ y) - [x, y] \in Z(R)$ for all $x, y \in L$.
ii) $F[x, y] - x \circ y \in Z(R)$ for all $x, y \in L$.
iii) $[F(x), d(y)] - [x, y] \in Z(R)$ for all $x, y \in L$.

Proof. i) By hypothesis,

$$F(x \circ y) - [x, y] \in Z(R) \text{ for all } x, y \in L. \tag{3}$$

Since $d(Z(L)) \neq (0)$, we choose fixed element $0 \neq z \in Z(L)$ which $d(z) \neq 0$. Also, $z, d(z) \in Z(R)$ from the Lemma 2.4. Replacing x by $2xz$ in Equation (3) and using $char(R) \neq 2$, we get

$$F((x \circ y)z + x[z, y]) - x[z, y] - [x, y]z \in Z(R) \text{ for all } x, y \in L$$

In this expression, using $z, d(z) \in Z(R)$ and Equation (3), we have

$$d(z)(x \circ y) \in Z(R) \text{ for all } x, y \in L$$

Hence, using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we obtain $x \circ y \in Z(R)$ for all $x, y \in L$. From the Lemma 3.2 we get $L \subseteq Z(R)$.

ii) By hypothesis,

$$F[x, y] - x \circ y \in Z(R) \text{ for all } x, y \in L. \tag{4}$$

Since $d(Z(L)) \neq (0)$, we choose fixed element $0 \neq z \in Z(L)$ which $d(z) \neq 0$. Also, $z, d(z) \in Z(R)$ from the Lemma 2.4. Replacing x by $2xz$ in Equation (4) and using $char(R) \neq 2$, we get

$$F(x[z, y] + [x, y]z) - (x \circ y)z - x[z, y] \in Z(R) \text{ for all } x, y \in L$$

In this expression, using $z, d(z) \in Z(R)$ and Equation (4), we obtain

$$d(z)[x, y] \in Z(R) \text{ for all } x, y \in L$$

Hence, using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we have $[x, y] \in Z(R)$ for all $x, y \in L$. From the Lemma 3.1 we get $L \subseteq Z(R)$.

iii) By hypothesis,

$$[F(x), d(y)] - [x, y] \in Z(R) \text{ for all } x, y \in L. \tag{5}$$

Since $d(Z(L)) \neq (0)$, we choose fixed element $0 \neq z \in Z(L)$ which $d(z) \neq 0$. Also, $z, d(z) \in Z(R)$ from the Lemma 2.4. Replacing y by $2yz$ in Equation (5) and using $char(R) \neq 2$, we get

$$[F(x), d(z)y + zd(y)] - [x, y]z - y[x, z] \in Z(R) \text{ for all } x, y \in L$$

In this expression, using $z, d(z) \in Z(R)$ and Equation (5), we get

$$d(z)[F(x), y] \in Z(R) \text{ for all } x, y \in L$$

By using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we have

$$[F(x), y] \in Z(R) \text{ for all } x, y \in L$$

Replacing y by x in above expression, we obtain $[F(x), x] \in Z(R)$ for all $x, y \in L$. From the Lemma 3.3 we get $L \subseteq Z(R)$. □

Theorem 3.6. *Let R be a prime ring with $char(R) \neq 2$, $0 \neq F : R \longrightarrow R$ be a right generalized reverse derivation with associated right reverse derivation d and*

L be a nonzero square closed Lie ideal of R such that $d(Z(L)) \neq (0)$. If one of the following conditions is satisfy, then $L \subseteq Z(R)$.

i) $[F(x), F(y)] - [x, y] \in Z(R)$ for all $x, y \in L$.
ii) $F(x) \circ F(y) - x \circ y \in Z(R)$ for all $x, y \in L$.
iii) $[F(x), F(y)] - x \circ y \in Z(R)$ for all $x, y \in L$.
iv) $F(x) \circ F(y) - [x, y] \in Z(R)$ for all $x, y \in L$.

Proof. *i*) By assumption,

$$[F(x), F(y)] - [x, y] \in Z(R) \text{ for all } x, y \in L. \tag{6}$$

Since $d(Z(L)) \neq (0)$, we choose fixed element $0 \neq z \in Z(L)$ which $d(z) \neq 0$. Also, $z, d(z) \in Z(R)$ from the Lemma 2.4. Replacing x by $2xz$ in Equation (6) and using $char(R) \neq 2$, we have

$$[d(z)x + zF(x), F(y)] - x[z, y] - [x, y]z \in Z(R) \text{ for all } x, y \in L$$

In this expression, using $z, d(z) \in Z(R)$ and Equation (6), we obtain

$$d(z)[x, F(y)] \in Z(R) \text{ for all } x, y \in L$$

By using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we have

$$[x, F(y)] \in Z(R) \text{ for all } x, y \in L$$

Replacing y by x in above expression, we get $[x, F(x)] \in Z(R)$ for all $x, y \in L$. From the Lemma 3.3 we get $L \subseteq Z(R)$.

ii) By assumption,

$$F(x) \circ F(y) - x \circ y \in Z(R) \text{ for all } x, y \in L. \tag{7}$$

Since $d(Z(L)) \neq (0)$, we choose fixed element $0 \neq z \in Z(L)$ which $d(z) \neq 0$. Also, $z, d(z) \in Z(R)$ from the Lemma 2.4. Replacing x by $2xz$ in Equation (7) and using $char(R) \neq 2$, we get

$$(d(z)x + zF(x)) \circ F(y) - (x \circ y)z - x[z, y] \in Z(R) \text{ for all } x, y \in L$$

In this expression, using $z, d(z) \in Z(R)$ and Equation (7), we obtain

$$d(z)(x \circ F(y)) \in Z(R) \text{ for all } x, y \in L$$

By using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we have

$$x \circ F(y) \in Z(R) \text{ for all } x, y \in L$$

Replacing y by x in above expression, we get $x \circ F(x) \in Z(R)$ for all $x, y \in L$. From the Lemma 3.4 we get $L \subseteq Z(R)$.

iii) By assumption,

$$[F(x), F(y)] - x \circ y \in Z(R) \text{ for all } x, y \in L. \tag{8}$$

Since $d(Z(L)) \neq (0)$, we choose fixed element $0 \neq z \in Z(L)$ which $d(z) \neq 0$. Also, $z, d(z) \in Z(R)$ from the Lemma 2.4. Replacing x by $2xz$ in Equation (8) and using $char(R) \neq 2$, we obtain

$$[d(z)x, F(y)] + [zF(x), F(y)] - xz \circ y \in Z(R) \text{ for all } x, y \in L$$

In this expression, using $z, d(z) \in Z(R)$ and Equation (8), we get

$$d(z)[x, F(y)] \in Z(R) \text{ for all } x, y \in L$$

By using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we have

$$[x, F(y)] \in Z(R) \text{ for all } x, y \in L$$

Replacing y by x in above expression, we have $[x, F(x)] \in Z(R)$ for all $x, y \in L$. From the Lemma 3.3 we get $L \subseteq Z(R)$.

iv) By assumption,

$$F(x) \circ F(y) - [x, y] \in Z(R) \text{ for all } x, y \in L. \tag{9}$$

Since $d(Z(L)) \neq (0)$, we choose fixed element $0 \neq z \in Z(L)$ which $d(z) \neq 0$. Also, $z, d(z) \in Z(R)$ from the Lemma 2.4. Replacing x by $2xz$ in Equation (9) and using $char(R) \neq 2$, we obtain

$$(d(z)x \circ F(y)) + (zF(x) \circ F(y)) - x[z, y] - [x, y]z \in Z(R) \text{ for all } x, y \in L$$

In this expression, using $z, d(z) \in Z(R)$ and Equation (9), we get

$$d(z)(x \circ F(y)) \in Z(R) \text{ for all } x, y \in L$$

By using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we have

$$x \circ F(y) \in Z(R) \text{ for all } x, y \in L$$

Replacing y by x in above expression, we have $x \circ F(x) \in Z(R)$ for all $x, y \in L$. From the Lemma 3.4 we get $L \subseteq Z(R)$. □

Theorem 3.7. *Let R be a prime ring with $char(R) \neq 2$, $0 \neq F : R \longrightarrow R$ be a right generalized reverse derivation with associated right reverse derivation d and*

L be a nonzero square closed Lie ideal of R such that $d(Z(L)) \neq (0)$. If one of the following conditions is satisfy, then $L \subseteq Z(R)$.

i) $[F(x), F(y)] - F[x,y] \in Z(R)$ for all $x, y \in L$.
ii) $F(x) \circ F(y) - F(x \circ y) \in Z(R)$ for all $x, y \in L$.
iii) $F[x,y] - [F(x), y] \in Z(R)$ for all $x, y \in L$.

Proof. *i*) For all $x, y \in L$, let

$$[F(x), F(y)] - F[x,y] \in Z(R) \tag{10}$$

By hypothesis, $d(Z(L)) \neq (0)$. Then, we choose fixed element $0 \neq z \in Z(L)$ which $d(z) \neq 0$. Also, $z, d(z) \in Z(R)$ from the Lemma 2.4. Replacing x by $2xz$ in Equation (10) and using $char(R) \neq 2$, we get

$$[d(z)x, F(y)] + [zF(x), F(y)] - F([x,y]z) \in Z(R) \text{ for all } x, y \in L$$

By using the fact that $z, d(z) \in Z(R)$ and Equation (10), we get

$$d(z)([x, F(y)] - [x,y]) \in Z(R) \text{ for all } x, y \in L$$

In this expression, using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we have

$$[x, F(y)] - [x,y] \in Z(R) \text{ for all } x, y \in L$$

Replacing x by $2d(z)y$ in above expression and using $char(R) \neq 2$, we obtain

$$d(z)[y, F(y)] \in Z(R) \text{ for all } x, y \in L$$

Again, using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we get

$$[y, F(y)] \in Z(R) \text{ for all } x, y \in L$$

From the Lemma 3.3 we obtain $L \subseteq Z(R)$.

ii) For all $x, y \in L$, let

$$F(x) \circ F(y) - F(x \circ y) \in Z(R) \tag{11}$$

By hypothesis, $d(Z(L)) \neq (0)$. Then, we choose fixed element $0 \neq z \in Z(L)$ which $d(z) \neq 0$. Also, $z, d(z) \in Z(R)$ from the Lemma 2.4. Replacing x by $2xz$ in Equation (11) and using $char(R) \neq 2$, we get

$$(d(z)x + zF(x)) \circ F(y) - F((x \circ y)z + x[z,y]) \in Z(R) \text{ for all } x, y \in L$$

By using the fact that $z, d(z) \in Z(R)$ and Equation (11), we have

$$d(z)(x \circ F(y) - x \circ y) \in Z(R) \text{ for all } x, y \in L$$

In this expression, using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we obtain

$$x \circ F(y) - x \circ y \in Z(R) \text{ for all } x, y \in L$$

Replacing y by $2yz$ in above expression and using $char(R) \neq 2$, we get

$$d(z)(x \circ y) \in Z(R) \text{ for all } x, y \in L$$

Again, using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we obtain

$$x \circ y \in Z(R) \text{ for all } x, y \in L$$

From the Lemma 3.2 we get $L \subseteq Z(R)$.

iii) For all $x, y \in L$, let

$$F[x, y] - [F(x), y] \in Z(R) \tag{12}$$

By hypothesis, $d(Z(L)) \neq (0)$. Then, we choose fixed element $0 \neq z \in Z(L)$ which $d(z) \neq 0$. Also, $z, d(z) \in Z(R)$ from the Lemma 2.4. Replacing y by $2yz$ in Equation (12) and using $char(R) \neq 2$, we get

$$F([x, y]z + y[x, z]) - [F(x), y]z - y[F(x), z] \in Z(R) \text{ for all } x, y \in L$$

By using the fact that $z, d(z) \in Z(R)$ and Equation (12), we have

$$d(z)[x, y] \in Z(R) \text{ for all } x, y \in L$$

In this expression, using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we obtain

$$[x, y] \in Z(R) \text{ for all } x, y \in L$$

From the Lemma 3.1 we get $L \subseteq Z(R)$. □

Theorem 3.8. *Let R be a prime ring with $char(R) \neq 2$, $0 \neq F : R \longrightarrow R$ be a right generalized reverse derivation with associated right reverse derivation d and L be a nonzero square closed Lie ideal of R such that $d(Z(L)) \neq (0)$. If one of the following conditions is satisfy, then $L \subseteq Z(R)$.*

i) $F[x, y] + [F(x), y] - [F(x), F(y)] \in Z(R)$ for all $x, y \in L$.
ii) $F[x, y] - F(x) \circ y - [d(y), x] \in Z(R)$ for all $x, y \in L$.

Proof. *i*) By assumption,

$$F[x,y]+[F(x),y]-[F(x),F(y)]\in Z(R) \text{ for all } x,y\in L. \tag{13}$$

Since $d(Z(L))\neq(0)$, we choose fixed element $0\neq z\in Z(L)$ which $d(z)\neq 0$. Also, $z,d(z)\in Z(R)$ from the Lemma 2.4. Replacing y by $2yz$ in Equation (13) and using $char(R)\neq 2$, we get

$$F[x,yz]+[F(x),yz]-[F(x),F(yz)]\in Z(R) \text{ for all } x,y\in L$$

In this expression, using $z,d(z)\in Z(R)$ and Equation (13), for all $x,y\in L$ we obtain

$$d(z)[x,y]+zF[x,y]+[F(x),y]z-d(z)[F(x),y]-z[F(x),F(y)]\in Z(R)$$

and from this

$$d(z)([x,y]-[F(x),y])\in Z(R) \text{ for all } x,y\in L$$

By using $0\neq d(z)\in Z(R)$ and Remark 2.1, we have

$$[x,y]-[F(x),y]\in Z(R) \text{ for all } x,y\in L$$

Replacing y by $2d(z)x$ in above expression and using $z,d(z)\in Z(R)$ and $char(R)\neq 2$, we have

$$d(z)[F(x),x]\in Z(R) \text{ for all } x,y\in L$$

Again, using $0\neq d(z)\in Z(R)$ and Remark 2.1, we get

$$[F(x),x]\in Z(R) \text{ for all } x,y\in L$$

From the Lemma 3.3 we get $L\subseteq Z(R)$.

ii) By assumption,

$$F[x,y]-F(x)\circ y-[d(y),x]\in Z(R) \text{ for all } x,y\in L. \tag{14}$$

Since $d(Z(L))\neq(0)$, we choose fixed element $0\neq z\in Z(L)$ which $d(z)\neq 0$. Also, $z,d(z)\in Z(R)$ from the Lemma 2.4. Replacing y by $2yz$ in Equation (14) and using $char(R)\neq 2$, we have

$$F[x,yz]-F(x)\circ yz-[d(yz),x]\in Z(R) \text{ for all } x,y\in L$$

In this expression, using $z,d(z)\in Z(R)$ and Equation (13), for all $x,y\in L$ we get

$$d(z)[x,y]+zF[x,y]-(F(x)\circ y)z-d(z)[y,x]-z[d(y),x]\in Z(R)$$

and from this

$$2d(z)[x,y] \in Z(R) \text{ for all } x,y \in L$$

By using $char(R) \neq 2$, $0 \neq d(z) \in Z(R)$ and Remark 2.1, we obtain

$$[x,y] \in Z(R) \text{ for all } x,y \in L$$

From the Lemma 3.1 we get $L \subseteq Z(R)$. □

Theorem 3.9. *Let R be a prime ring with $char(R) \neq 2$, $0 \neq F, G : R \longrightarrow R$ are right generalized reverse derivations with associated right reverse derivation d and g respectively, L be a nonzero square closed Lie ideal of R such that $d(Z(L)) \neq (0)$ and $g(Z(L)) \neq (0)$. If one of the following conditions is satisfy, then $L \subseteq Z(R)$.*

i) $[F(x), G(y)] - [x,y] \in Z(R)$ *for all* $x,y \in L$.
ii) $F[x,y] - [y, G(x)] \in Z(R)$ *for all* $x,y \in L$.
iii) $F(x \circ y) - y \circ G(x) \in Z(R)$ *for all* $x,y \in L$.

Proof. *i*) For all $x,y \in L$, let

$$[F(x), G(y)] - [x,y] \in Z(R) \tag{15}$$

By hypothesis, $d(Z(L)) \neq (0)$. Then, we choose fixed element $0 \neq z \in Z(L)$ which $d(z) \neq 0$. Also, $z, d(z) \in Z(R)$ from the Lemma 2.4. Replacing x by $2xz$ in Equation (15) and using $char(R) \neq 2$, we get

$$[d(z)x, G(y)] + [zF(x), G(y)] - x[z,y] - [x,y]z \in Z(R) \text{ for all } x,y \in L$$

By using the fact that $z, d(z) \in Z(R)$ and Equation (15), we obtain

$$d(z)[x, G(y)] \in Z(R) \text{ for all } x,y \in L$$

In this expression, using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we have

$$[x, G(y)] \in Z(R) \text{ for all } x,y \in L$$

Replacing y by x in above expression, we have $[x, G(x)] \in Z(R)$ for all $x,y \in L$. From the Lemma 3.3 we get $L \subseteq Z(R)$.

ii) For all $x,y \in L$, let

$$F[x,y] - [y, G(x)] \in Z(R) \tag{16}$$

By hypothesis, $d(Z(L)) \neq (0)$. Then, we choose fixed element $0 \neq z \in Z(L)$ which $d(z) \neq 0$. Also, $z, d(z) \in Z(R)$ from the Lemma 2.4. Replacing y by $2yz$ in Equation

(16) and using $char\,(R) \neq 2$, we get

$$F([x,y]z + y[x,z]) - y[z,G(x)] - [y,G(x)]z \in Z(R) \text{ for all } x,y \in L$$

By using the fact that $z, d(z) \in Z(R)$ and Equation (16), we get

$$d(z)[x,y] \in Z(R) \text{ for all } x,y \in L$$

In this expression, using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we have

$$[x,y] \in Z(R) \text{ for all } x,y \in L$$

From the Lemma 3.1 we obtain $L \subseteq Z(R)$.

iii) For all $x, y \in L$, let

$$F(x \circ y) - y \circ G(x) \in Z(R) \tag{17}$$

By hypothesis, $d(Z(L)) \neq (0)$. Then, we choose fixed element $0 \neq z \in Z(L)$ which $d(z) \neq 0$. Also, $z, d(z) \in Z(R)$ from the Lemma 2.4. Replacing y by $2yz$ in Equation (17) and using $char\,(R) \neq 2$, we get

$$F((x \circ y)z - y[x,z]) - (y \circ G(x))z - y[z,G(x)] \in Z(R) \text{ for all } x,y \in L$$

By using the fact that $z, d(z) \in Z(R)$ and Equation (17), we obtain

$$d(z)(x \circ y) \in Z(R) \text{ for all } x,y \in L$$

In this expression, using $0 \neq d(z) \in Z(R)$ and Remark 2.1, we have

$$x \circ y \in Z(R) \text{ for all } x,y \in L$$

From the Lemma 3.2 we get $L \subseteq Z(R)$. □

Example 3.10. *Let* $R = \left\{ \begin{pmatrix} x & y \\ 0 & x \end{pmatrix} \mid x,y \in \mathbb{Z} \right\}$ *and* $L = \left\{ \begin{pmatrix} 0 & a \\ 0 & 0 \end{pmatrix} \mid a \in \mathbb{Z} \right\}$, *where* $\mathbb{Z}$ *is the set of all integers. We define the mappings* $F, d : R \to R$ *as following:*

$$F\begin{pmatrix} x & y \\ 0 & x \end{pmatrix} = \begin{pmatrix} -x & 0 \\ 0 & -x \end{pmatrix} \quad , \quad d\begin{pmatrix} x & y \\ 0 & x \end{pmatrix} = \begin{pmatrix} 0 & y \\ 0 & 0 \end{pmatrix}$$

It is easy to show that, L is square closed Lie ideal of ring R, d is right reverse derivation and F is right generalized reverse derivation with associated d. Moreover, since $\begin{pmatrix} 0 & a \\ 0 & 0 \end{pmatrix} \in Z(L)$ *and* $d\begin{pmatrix} 0 & a \\ 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & a \\ 0 & 0 \end{pmatrix} \neq \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$ *for any* $0 \neq a \in \mathbb{Z}$, *condition* $d(Z(L)) \neq (0)$ *is satisfied.*

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REMOVAL OF OCHRATOXIN A FROM RED WINE BY USING RED KIDNEY BEAN PEEL

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ABSTRACT

Present study was performed to reduce the OTA (ochratoxin A) levels of red wine by using red kidney bean peel as adsorbent. The adsorption studies were evaluated by adsorption isotherm, kinetic models. The adsorption data conformed to the Freundlich isotherm and pseudo-second-order kinetic model with respect to the correlation coefficients. The adsorption equilibria of OTA for real wine sample and OTA synthetic solution were almost established within 240 and 300 min, respectively. The removal efficiency was decreased by increasing temperature. Thermodynamic parameters indicated that adsorption process was spontaneous, exothermic, chemical and the randomness was decreased. The removal percent of polyphenols and anthocyans were lower at lower adsorbent masses. This data was useful to develop an environmentally friendly process to remove OTA from red wine at low amount of OTA, without affecting wine quality parameters.

1. INTRODUCTION

Ochratoxins are a group of mycotoxins produced mainly by strains of some *Aspergillus* and *Penicillium* species. Their structures imply the linking between two moieties; a substituted dihydroisocoumarin and L-phenylalanine. The family of ochratoxins consists of three members, A, B, and C, which differ slightly from each other in chemical structures. Ochratoxin A (OTA) was first reported in South Africa as a secondary metabolite produced by a strain of Aspergillus ochraceus (Van der Merwe et al., 1965). This mycotoxin has been shown to be nephrotoxic, hepatotoxic, teratogenic and carcinogenic to animals and has been classified as a possible carcinogen to humans (Castegnaro et al., 1998, Pfohl-Leszkowicz et al., 1998, Bacha et al., 1993, Nikolov et al., 1996, Radic et al., 1997). The chemical structure of Ochratoxin A is (R-N-[(5-chloro-3, 4-dihydro-8-hydroxy-3-methyl-1-oxo-1H-2-benzopyran-7-yl) carbonyl] phenylalanine) (Figure 1).

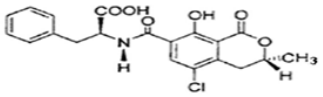

Figure 1. The chemical structure of OTA.

OTA occurs in a variety of foods, including beer, wine, vinegar, grape juice, coffee, cocoa, pulses, spices, dried fruits and meats. The presence of OTA, especially in wine, is believed to be a risk factor for human health. Since 2001, the European Union has established a regulation, which was revised some times, including maximum levels for commercial wines and grape juice (2 μg/L), and dried vine fruits (10 μg/kg) among others (Commission Regulation, 2006). Due to the high toxicity of OTA, many methods to control their effects have been proposed. One of the methods is based on the adsorption of OTA by several organic and inorganic materials. In this study, red kidney bean peel was used as adsorbent for reducing OTA level in a commercial red wine. It is a promising method for removing OTA by using household wastes. Red kidney bean peel was interacted with OTA by Van der Walls interaction, hydrogen bonding and electrostatic forces. These attractions led up to a high removal OTA capacity. Adsorption by using household waste as adsorbent have advantages according to attainability, inexpensiveness and simple proceeding.

The target of this work was performing OTA adsorption onto red kidney bean peel, evaluated the data by using adsorption isotherms, kinetics and comparing adsorption data obtained from synthetic solution and red wine.

2. MATERIAL AND METHODS

2.1. Reagents and Materials

The OTA standard was purchased from Sigma-Aldrich (St. Louis, MO). All solvents were high-performance liquid chromatography (HPLC) grade. Methanol was from Panreac (Barcelona, Spain), acetic acid was from Carlo-Erba (Milano, Italy), acetonitrile was from Sigma-Aldrich, and ultrapure water was obtained from a Milli-Q apparatus (Millipore, Molsheim, France). OTA stock solution (1000 ng/mL) was prepared in methanol.

Red kidney bean peel used as adsorbent was obtained from agricultural land in Izmir-Turkey. Firstly, the peels were washed with distilled water and then preheated in an oven at 100 - 110 °C for about 24 h to reduce the moisture content. The dried slices were ground by using grinder and sieved to obtain a particle size range of 0.5–1mm and stored in plastic bottle for further use. No other chemical or physical treatments were used prior to adsorption experiments.

2.2. FTIR Analysis of red kidney bean peel

To clarify the functional groups of adsorbent, the infrared spectrum was obtained with a FTIR (Perkin Elmer Spectrum BX-II) spectrophotometer with a pellet of powdered potassium bromide and adsorbent. Infrared spectra were carried out in the region of 4000–400 cm-1. The FTIR spectrum of adsorbent was shown in Figure 2. It was shown that the bands corresponding to the functional groups of O-H stretching vibration (3430 cm−1), C-H aromatic and aliphatic stretching vibration (2925 cm−1), C=O stretching vibration (1730-1630 cm−1), C=C aromatic stretching vibration (1600 and 1500 cm−1), C-H deformation vibration (1465 and 1378 cm−1) and C-O stretching vibration (1040 cm−1) were observed (Estevin et al., 2006). The bands of O-H groups, C =O stretching and -C-C group (880cm-1)

in the spectrum indicated the possible involvement of that functional group on the surface of red kidney bean peel in OTA adsorption process. These groups helped to form the interaction between the red kidney bean peel and OTA.

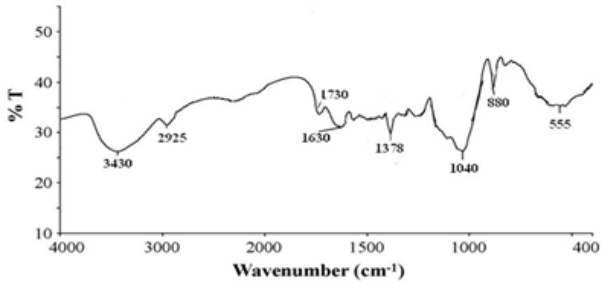

Figure 2. FTIR spectrum of red kidney bean peel.

2.3. Adsorption Studies for Synthetic OTA Solutions

The effect of adsorbent dose on the amount of OTA adsorbed from synthetic solution was obtained by contacting 25mL of OTA solution of initial concentration of 100 ng/L with different amount of red kidney bean peel (0.005-0.100 g) into a number of 50 mL glass bottles at pH 3.48. The bottles were placed in a temperature controlled shaker at 298 K until reaching equilibrium. The agitation was provided at 150 rpm. Then, each test solution was centrifuged at 4000 rpm for 15 min. One milliliter of each supernatant was used for OTA analysis.

The contact time of adsorbents, the adsorption experiments were performed with 25 mL of 100 ng/mL OTA synthetic solutions at various time intervals for 540 min with 0.25 g of red kidney bean peel (RKB) at pH of 3.50. These data were used to clarify the adsorption kinetics. Equilibrium studies were performed by contacting fixed amount of red kidney bean peel (0.25 g) with 25 mL of synthetic OTA solution of different initial concentrations(1.5, 3, 5, 10, 25, 50, 100, 125, 250, and 500 ng/L) in 50mL glass bottles at a temperature of 298 K and pH of 3.50. The initial and equilibrium concentrations of OTA were analyzed using Agilent Technologies 1100 (Heilbron, Germany) series liquid chromatographic system equipped with a fluorescence at 333 (excitation) and 458 nm (emission), controlled by Chemstation 3D software. The amount of adsorption at equilibrium, qe (mg/g), was calculated by Eq. (1).

$$q_e = (C_0 - C_e)\frac{V}{M}$$

where C_o and C_e (mgL^{-1}) are the liquid-phase concentrations of OTA at initial and equilibrium, respectively. V is the volume of the solution (L) and M is the mass of dry sorbent used (g). The percentage removal of synthetic OTA solution (R %) was calculated by using Eq.(2).

$$R\% = (C_0 - C_e)/C_0 x100 \qquad (2)$$

The effect of temperature on the adsorption of OTA onto 0.25g of RKB was investigated at six different temperatures (298, 303, 308, 313 and 318K) using 25mL initial concentration of 100 ng/mL OTA synthetic solutions.

To different amounts (0.1g, 0.25g, 0.5g, 0.75g and 1.0g) of each adsorbent, 10mL of red wine sample was added to reveal the adsorbent amount effect for real wine sample. The batch adsorption studies were performed as procedure for synthetic OTA solution for 0.25 g of RKB. Total polyphenol and total anthocyan contents were determined for wine before and after batch adsorption process by using Shimadzu UV 1601 (Kyoto, Japan) series spectrophotometric system at 280 and 520 nm, respectively (Gonzalez-Rodriguez et al., 2002).

2.4. OTA Analysis

HPLC analyses were performed on an Agilent Technologies 1100 (Heilbron, Germany) series liquid chromatographic system equipped with a fluorescence at 333 (excitation) and 458 nm (emission) controlled by Chemstation 3D software. The chromatographic conditions were follows: C18 reverse phase (250 mmx4mm, 5 μm) HPLC analytical column; volume of injection, 20 μL loop; isocratic elution (water/acetonitrile/acetic acid, 48.5:50.5:1, v/v/v); flow rate, 1.5 mL/min; and temperature, 50 ℃. An aliquot of the original OTA test solution was used as the HPLC standard.

The calibration curve of OTA ranged from 1.0 to 10.0 ng/mL with an equation of y=0.1985x+0.0812 with the regression coefficient R2=0.9993. The direct injection method was applied to the analysis of the red wine sample (Dall'Asta et al., 2004). The supernatant containing OTA in adsorption experiments was collected in a vial, evaporated to dryness under an N2 stream, and redissolved in the HPLC mobile phase. The limit of detection for OTA was 0.20 ng/mL; the limit of quantification was 1.15 ng/mL; the reproducibility of interday and intraday for 2.0 ng/mL was 2.68 and 3.75%, respectively.

3. RESULTS AND DISCUSSION

3.1. Effect of Contact Time

Figure 3 indicated the effect of contact time onto adsorption of OTA by using synthetic OTA solution and real wine sample. It was concluded that the adsorption behavior was similar for adsorption by using synthetic OTA solution and real red wine. Furthermore, equilibrium removal efficiency for real red wine (91%) was lower than the synthetic one (94%). Additionally, adsorption onto RKB was rapid for the first 120 min and thereafter it proceeded at a slower rate and finally reached saturation. The contact time was nearly 240 min for synthetic OTA solution and 300 min for real red wine. The batch adsorption studies were carried out for 300 min for synthetic and real sample. The adsorption for real red wine took relatively longer contact time to attain equilibrium due to interference of the polyphenols with the adsorption of OTA.

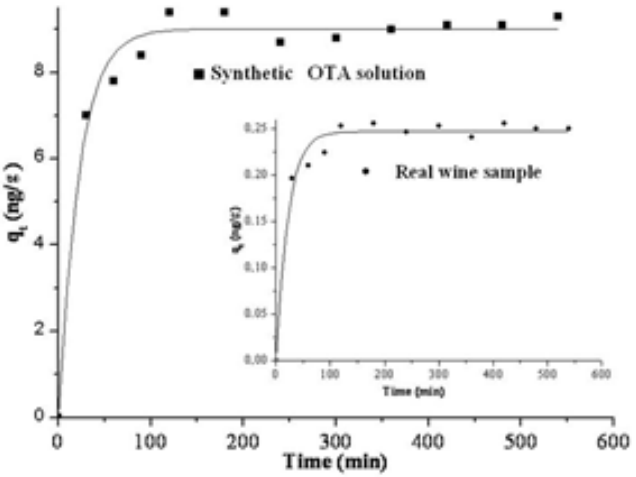

Figure 3. Effect of contact time for the adsorption of OTA in synthetic solution at pH 3.5 (C0 =100 ngmL-1) and in real red wine (C0 =2.8 ngmL-1) at 298K.

3.2. Effect of adsorbent dose on OTA adsorption

From the Figure 4, it was observed that uptake per unit mass of red kidney bean peel decreased for both real red wine and synthetic OTA solution by increasing mass of adsorbent. Furthermore, the percentage of OTA removal increased from 86.0 to 94.0% with an increase in adsorbent mass from 0.005 to 0.100 g for synthetic OTA solution. When the percentage of the removal increased with the dosage increase of RKB, the uptake per unit mass decreased. This result was attributed to the availability of more adsorption sites by increasing the mass of adsorbent and some of the adsorption sites remain unsaturated during the adsorption process. The batch adsorption data were collected by using 0.25g of RKB.

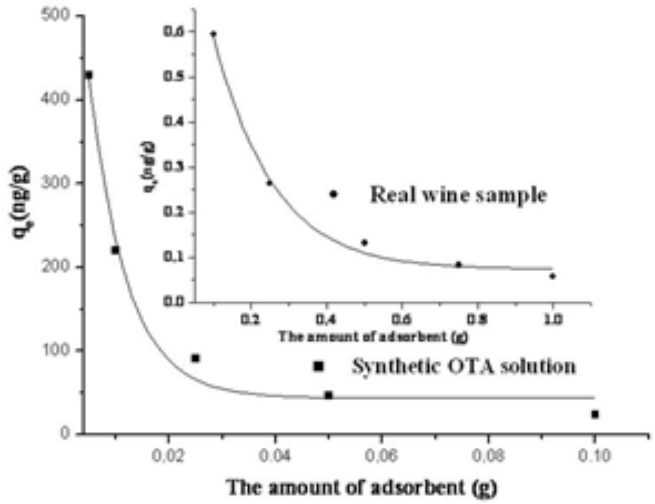

Figure 4. Effect of adsorbent mass for the adsorption of OTA in synthetic solution at pH 3.5 (C0 =100 ngmL-1) and in real red wine (C0 =2.8 ngmL-1) at 298K.

3.3. Adsorption Isotherms

The adsorption isotherms clarified the specific relation between the concentration of the adsorbate and its adsorption degree onto adsorbent surface at a constant temperature. To reveal the adsorption capacity of red kidney bean peel for the removal of OTA in synthetic OTA solution, the Langmuir and Freundlich isotherm models were used and the isotherms were shown in Figure 5. The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogenous adsorbent surface (Langmuir, 1916). A basic assumption is that sorption takes place at specific homogeneous sites within the adsorbent. Once an OTA molecule occupies a site, no further adsorption can take place at that site. The linear form of Langmuir isotherm is (Langmuir, 1916):

$$\frac{C_e}{q_e} = \frac{1}{C_m a_L} + \frac{C_e}{C_m} \tag{3}$$

where q_e is the amount adsorbed at equilibrium (ng/g), C_e is the equilibrium concentration of the adsorbate (ng/L), and C_m (ng/g) and a_L are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and the slope of the linear plot of experimental data of C_e/q_e versus C_e. The values of constants C_m and a_L were -24.5 ng/g and -0.02, respectively. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L (Hall et al., 1966), also known as the separation factor, given by:

$$R_L = \frac{1}{\left(1 + a_L C_0\right)} \tag{4}$$

The value of R_L lies between 0 and 1 for favourable adsorption, while $R_L > 1$ represents unfavourable adsorption, and $R_L = 1$ represents linear adsorption while the adsorption process is irreversible if $R_L = 0$. C_0 (the initial OTA concentration mmol L^{-1}) and a_L were used to calculate the dimensionless constant separation factor. The dimensionless parameter R_L remained among 1.03 to 2.10 ($R_L>1$) for initial concentration 1.5 -25ng/L indicated the unfavorable adsorption process. Favorability of adsorption for high initial concentration (C_0=50-500ng/L) was not revealed out because of $R_L <0$. The applicability of the isotherm models to the adsorption data was inferred by the correlation coefficient, R^2 value of Langmuir and Freundlich plots. The higher the R^2 value, the better the fit. The correlation coefficient of Langmuir isotherm plot ($R_l^2=0.79$) was lower than the correlation coefficient of Freundlich isotherm plot ($R_f^2=1.0$). These results indicated that adsorption data did not correspond the Langmuir isotherm model.

The Freundlich isotherm (Freundlich, 1906) is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces and adsorption capacity is related to the concentration of OTA at equilibrium.

$$q_e = K_f C_e^{\,n_f} \tag{5}$$

$$\ln q_e = \ln K_f + n_f \ln C_e \quad (6)$$

where K_f is roughly an indicator of the adsorption capacity and n_f is the adsorption intensity. The magnitude of the exponent, n_f, gives an indication of the favorability of adsorption. Values of $n_f > 1$ represent unfavorable adsorption condition. The values of K_f and n_f for Freundlich isotherm were 0.534ng/g and 1.13, respectively. Freundlich isotherm model exhibited better fit compared to the Langmuir model. The isotherm parameters were summarized in Table 1. The fact that this occurred may be due to a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. Furthermore, multilayer adsorption was occurred due to the presence of energetically heterogeneous adsorption sites. The heterogeneity arises from the presence of different functional groups on the surface, and the various adsorbent–adsorbate interactions (Hameed and El-Khaiary, 2008).

In fact, OTA is a weak acid partially dissociated at the pH of wine and carries a negative charge. Red kidney bean peel was protonated in acidic medium (pH=3.5) for that reason the negative moiety of OTA might be pulled by protanated regions. The carboxyl group of phenyalanine moiety onto OTA helped for higher removal.

Additionally, the adsorption data were collected for red wine sample. The polyphenols interfere with the adsorption of OTA by adsorbents (Sims et al., 1995, Aleixandre et al., 1996, Manfredini, 1989). The interference effect of the organic components of wine onto adsorption were clarified through performing polyphenols and anthocyans adsorption by using 0.10; 0.25; 0.50; 0.75 and 1.00 g of RKB. The removal percent of polyphenols and anthocyans were lower by comparing with the removal percent of OTA (Table 2). This was favorable result and the red kidney bean peel is an alternative adsorbent for removing OTA. The removal percentage was increased by using 0.10 to 0.25 g of adsorbent for red wine sample, after than it was remained at 94% for 0.50 g of adsorbent and the percentage was decreased by the amount of adsorbent increase to 1.00 g. At lower adsorbent dosage, the removal percentage of OTA was higher than the removal percentage of organic components. At higher adsorbent dosage, the adsorption behavior was changed and OTA and the other organic components competed to the surface of red kidney bean peel. Consequently, 1.00 g of RKB had disadvantage because of removing more organic components.

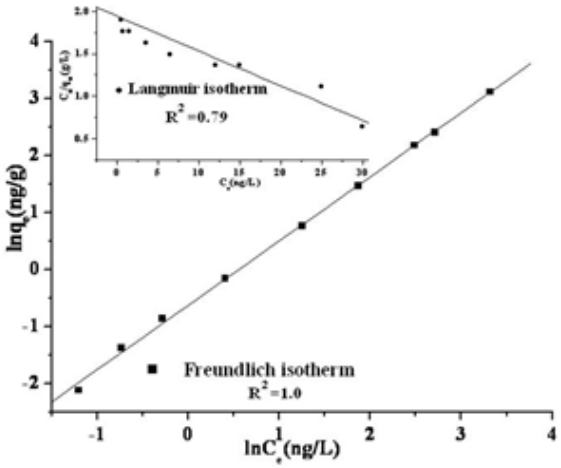

Figure 5. Langmuir and Freundlich isotherm plots for OTA adsorption onto red kidney bean peel at 298K (pH=3.5).

Table 1. Isotherm parameters for OTA adsorption onto red kidney bean peel

Langmuir parameters			**Freundlich parameters**		
C_m**(ng/g)**	a_L	R_l^2	K_f**(ngmL^{-1}(Lng^{-1})^{nf})**	n_f	R_f^2
-24.478	-0.021	0.79	0.5336	1.126	1.0

Table 2. Adsorption percent of polyphenols and anthocyans by using different adsorbent amount

Organic component	**Adsorption (%)**				
	Amount of adsorbent (g)				
	0.10	**0.25**	**0.50**	**0.75**	**1.00**
Total polyphenols, 280 nm	10	11	18	39	82
Total anthocyans, 320nm	12	18	35	58	100

3.4. Adsorption kinetics

In order to analyze the sorption kinetics of OTA on red kidney bean peel, the pseudo-first-order and pseudo-second-order kinetic models were applied to the experimental data. Lagergren proposed a method for adsorption analysis which is the pseudo-first-order kinetic equation of Lagergren (Lagergren, 1898) in the form:

$$\frac{1}{q_t} = \left(\frac{k_1}{q_1}\right)\left(\frac{1}{t}\right) + \left(\frac{1}{q_1}\right) \qquad (7)$$

where q_t is the amount of OTA uptaken at different times t (ng g^{-1}), k_1 is rate constant for pseudo-first-order kinetics of OTA uptake (min^{-1}), t is the time (min), q_1 maximum adsorption capacity (ng g^{-1}). The linear plot of $1/q_t$ versus t was obtained. The values of q_1 and k_1 can be estimated from the slope and intercept of the plots for synthetic OTA solution and red kidney bean peel. In many cases the first-order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes (McKay and Ho, 1999).

The pseudo-second-order equation based on equilibrium adsorption (Ho and McKay, 1978) is expressed as

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_2^{\,2}} + \frac{t}{q_2} \tag{8}$$

where k_2 is the rate constant (gng^{-1} min^{-1}), q_2 is the maximum adsorption capacity (ngg^{-1}) for the pseudo-second-order adsorption kinetic model. To calculate the values of k_2 and q_2 for both synthetic OTA solution and red wine sample, the intercept and the slope of the linear plots of (t/q_t) versus t were obtained. The first and second-order rate constants values were summarized in Table 3. It was concluded from Table 2 that the correlation coefficients for the pseudo-first-order kinetic model obtained for synthetic OTA solution and red wine were low. Additionally, the pseudo second kinetic model was appropriate for adsorption of OTA onto red kidney bean peel. For synthetic OTA solution the correlation coefficients for pseudo-first and second order kinetics models and q_l and q_2 values nearly same. Further more for real red wine, the correlation coefficient of pseudo-second-order kinetic model was higher than the correlation coefficients of pseudo-first-order kinetic model. This suggests that this sorption system was not a first-order. It was assumed that the adsorption onto RKB might be chemically with respect to pseudo-second- order kinetic model.

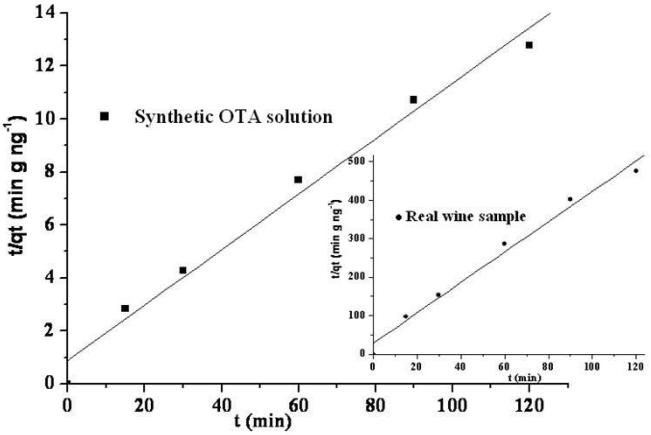

Figure 6. Pseudo-second order sorption kinetics of OTA onto red kidney bean peel at 298K (pH= 3.5).

Table 3. Kinetic parameters of OTA adsorption onto red kidney bean peel for synthetic OTA solution and real wine sample

	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	q_1(ng g^{-1})	k_1(min^{-1})	R_1^2	q_2(ng $g^{-1)}$	k_2(gng^{-1} min^{-1})	R_2^2
Synthetic OTA solution	9.883	12.999	0.982	9.611	0.012	0.984
Real wine sample	0.256	9.857	0.962	0.253	0.558	0.986

3.5. Adsorption thermodynamics

The amounts of sorption of OTA by RKB were measured at temperatures 298, 303, 308, 313 and 318 K to identify the adsorption thermodynamic. The thermodynamic parameters including Gibbs free energy change (ΔG°), enthalpy (ΔH°), and entropy change (ΔS°), have a significant role to determine the feasibility, spontaneity and heat change for the adsorption process. Thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) change of adsorption can be evaluated by using following equations (Smith and Van Ness, 1987, Ho et al., 2002):

$$\Delta G^\circ = -RT \ln K_c \tag{9}$$

$$K_c = \frac{C_s}{C_e} \tag{10}$$

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{11}$$

where C_s is the concentration of OTA adsorbed (ng/L); C_e is the equilibrium concentration (ng/L) at a given temperature; T is the solution temperature in K; K_c is the equilibrium constant; and R is the gas constant (8.314 J K^{-1} mol^{-1}). The enthalpy (ΔH°), and entropy change (ΔS°) of adsorption were estimated from van't Hoff equation (Eq. 11) plotting lnK_c versus 1/T. Thermodynamic parameters were summarized in Table 4.

Table 4. Thermodynamic parameters for OTA adsorption onto red kidney bean peel

***T*(K)**	***K_c***	**ΔG°(kJmol^{-1}K^{-1})**	**ΔH°(kJmol^{-1})**	**ΔS° (Jmol^{-1}K^{-1})**
298	2.75	-6.82		
303	2.59	-6.52		
308	1.39	-3.55	-121.7	-384.2
313	0.02	-1.16		
318	0.01	-0.03		

The negative values of ΔG° in the temperature range of 298–318K were due to the fact that the adsorption process was spontaneous and feasible thermodynamically. The negative value of ΔG° has increased from −6.82 to −0.03 kJmol^{-1}K^{-1} with an increase in temperature from 298 to 318K, indicated that the spontaneous nature was inversely proportional to the temperature. This result indicated that adsorption of OTA onto RKB became less favourable at higher temperature. The negative value of ΔH° (-121.7 kJ mol^{-1}) suggested that the exothermic nature of OTA sorption while the negative value of ΔS° (-384.2 J mol^{-1} K^{-1}) indicated that the decreasing randomness at the solid/solution interface during the adsorption of OTA onto red kidney bean peel for synthetic OTA solution. Furthermore, the magnitude of ΔH° gives an idea about the type of sorption. The heat of physical adsorption (van der Waals adsorption) of gases is relatively low, in the order of 1–5 kcal mol^{-1} (4–21 kJ mol^{-1}), whereas that of chemisorption is much higher, of a magnitude of 24–120 kcal mol^{-1} (100–500 kJ

mol^{-1}) comparable to that for a chemical union (Shaw, 1970; Giles et al., 1960). The adsorption of OTA onto RKB was almost a chemical process. This result was also supported with suitability of the adsorption kinetic to pseudo-second order kinetic model.

4. CONCLUSION

The results demonstrated that Ochratoxin A can be effectively removed from wine by using red kidney bean peel as adsorbent and this procedure was economical and environmentally friendly technique because of recycling of household wastes. The adsorption process was performed with high removal percentage of OTA and low removal percentage of total polyphenols and anthocyans at less dosage of red kidney bean peel. The adsorption behavior for real wine sample and synthetic OTA solution were similar. The components of red wine might not excessively affect the efficiency of OTA reduction. Consequently, this study enlightens the production process of wine for reducing the amount of OTA.

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EUROPEAN TEMPUS TATU PROJECT AND WIRESHARK SOFTWARE IN INDUSTRIAL NETWORKS DATA TRANSFER PROTOCOLS STUDYING AND ANALYZING[*]

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ABSTRACT

Industrial data transfer technologies are implementing in industry, transport, energetic together with Industry 4.0 and IIoT concepts. Compatible with previous generations TCP/IP based protocols ProfiNet, ModBus/TCP, Ethernet/IP, EtherCAT were created to perform com-plex technical systems remote control.

In 2013 – 2017 European TEMPUS TATU (Trainings in Automation Technologies for Ukraine) project was realized and TATU Smart Lab (TSL) equipment was obtained.

TSL is a set of devices for modern automation technologies studying. It matches to Indus-try 4.0 and IIoT concepts. It contains programmable logic controllers, I/O devices, switches, wireless access points and can be used for studying of Ethernet based data transfer technolo-gies, wireless data transfer, TCP/IP technologies, hard real-time systems, EtherCAT, CAN, RS232/485, PROFINET, Modbus TCP interfaces.

WIRESHARK software allows to analyze network traffic and supports capturing of long network protocols list. It helps to understand the reason of network problems, simplifies indus-trial and corporate networks exploitation.

1. INTRODUCTION

During last 5-7 years in industry, at the different kinds of transport, in energetic field, etc. are very actively implementing data exchange technologies between separate devices, device groups and networks. These technologies based on Industry 4.0 (4th industrial revolution), IoT (Internet of Things), IIoT (Industrial Internet of Things) concepts. In accordance with these concepts a lot of different devices became smart, possessing of own CPUs, memory and different wired and wireless interfaces for external data exchange. Some of them (like complex PLCs) allow to unite different industrial network segments, having sufficient productivity and much lower cost compared to computers (Shapo, URL-1, 2017).

[*] This study is the revised version of the same name paper presented in the "2nd International Rating Academy Congress: Hope" held in Kepez / Çanakkale on April 19-21, 2018.

From the beginning of 90th years of 20th century in industry are very popular some protocols and data transfer technologies, most known are ASI, ProfiBus, FieldBus, HART, ModBus, CAN family, BAC, etc. But in connection with Internet development and forthcoming of absolutely new challenges were created some TCP/IP based protocols, which allow to perform remote control of complex technical systems for enhancement of control quality, decreasing response time for force majeure situations and cost for control and exploitation of such systems. Protocols ProfiNet, ModBus/TCP, Ethernet/IP, EtherCAT became well known; they are compatible with previous generations, but allow to solve fundamentally new tasks. But in some situations by cost/productivity ratio win protocols and technologies, which don't have wide spread, but firmly hold theirs niche. Some of them are described below.

2. MAIN TEXT

ACN (Architecture for Control Networks) is network control protocol, initially destined for entertainment industry (URL-2, 2017). It has open source code and maintains some subordinate protocols (table 1).

AYIYA (Anything In Anything) is network protocol for tunneling between IP-networks and controlling there (URL-3, 2017). Very often it's used for IPv6 packets transit through the networks based on IPv4 protocol. Network security is provided with absence of addresses and content of tunneled packets falsification possibility. At least one of two tunnel endpoints allows mobile devices connecting.

Table 1. ACN protocols family and corresponding standards

Protocol	Standard
Root Layer, Session Data Transport and Device Management Protocols, Device Description Language	ANSI E1.17
Service Location Protocol (SLP)	RFC 2609
Simple Network Time Protocol (SNTP)	RFC 2030, ANSI E1.30-3-2009
Trivial File Transfer Protocol (TFTP)	RFC 1350
Streaming ACN (sACN)	ANSI E1.31
RDM Extension (RDMNet)	ANSI E1.33
Remote Device Management (RDM)	ANSI E1.20

CIP (Common Industrial Protocol) is the set of standards (URL-4, 2017), which are maintained by Open DeviceNet Vendors Association (ODVA). CIP extensions are CIP safety, CIP Sync and CIP Motion protocols. CIP contains full set of requirements and possibilities for complex automation systems and their subsystems development from following sides: control, information security, motion organizing, informing. Some most important protocols and industrial data transfer technologies are based on CIP as well and briefly described below.

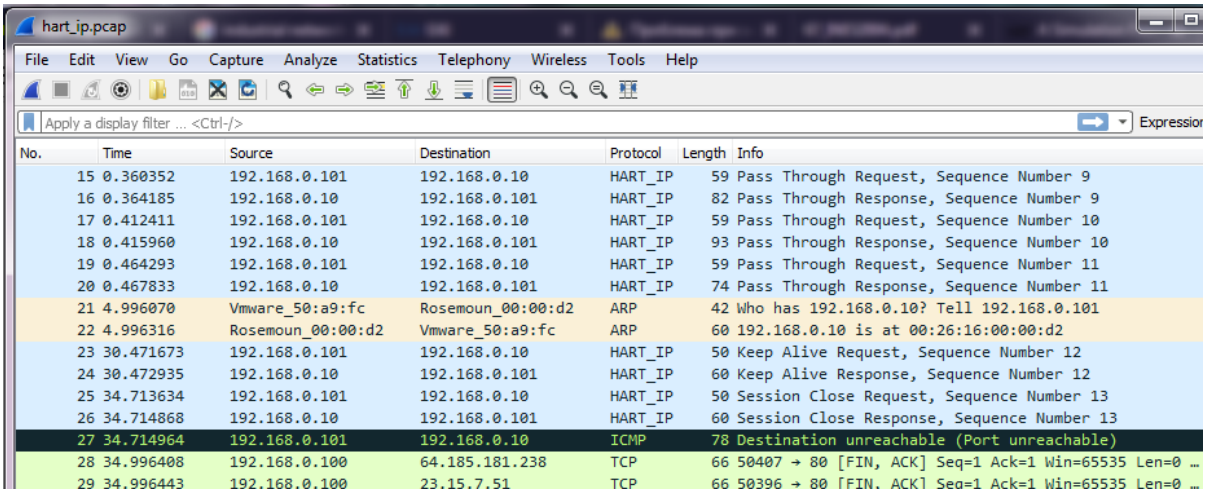
EtherNet/IP is open industry protocol, which uses standard Ethernet chips and cable systems, based on IEEE 802.3 standard, and serve for input/output real time data exchange and information messages in DeviceNet and ControlNet industrial networks. CIP provides common application level between networks, which doesn't depend on media (cable system). It allows to perform direct routing CIP messages in EtherNet/IP, ControlNet and DeviceNet. Depending on application requirements EtherNet/IP network may be stand-alone or combined with DeviceNet or ControlNet networks for additional flexible information and control services realization. EtherNet/IP transfers big user, configuration and input/output data volumes in the same high-speed network; tightly associates technological and corporate operations; facilitates technical maintenance expenses decreasing thanks to existing network

resources and technical facilities using; allows to commercial and industrial technological levels to coexist in the same network; works with TCP/IP and HTTP protocols.

DNP3 (Distributed Network Protocol, version 3) is a set of communication protocols (URL-5, 2017), which are used for data transfer between components in automation systems like different types of equipment for data acquisition and control and described in IEEE 1815 standard. In SCADA systems DNP3 is used by SCADA master stations (control centers), Remote Terminal Units (RTU) and different Intelligent Electronic Devices (IED). It uses 3 levels of OSI model (data link, transport, application) and contains Secure Authentication v5 mechanism, which allows to master or remote DNP3-system uniquely determine, that connection is established with legitimate user or host, but not with malicious user.

HART-IP (Highway Addressable Remote Transducer) protocol (URL-6, 2017) based on standard Ethernet IEEE 802.3 hardware and cable systems and with Wi-Fi IEEE 802.11 equipment, that's why it's possible to use it with standard network switches, routers, access points. It may be used in redundant mesh or ring topologies and with PoE (Power over Ethernet) power supply standard by twisted pair. Possible data transfer rates are 10 or 100 Mbps and 1 Gbps. HART network, including devices working with Wireless HART protocol, is compatible with office and industrial LAN-switches, fiber optics media converters, Wi-Fi access points and another equipment. Compatibility with classic HART protocol allows to put corresponding gateways into action and to work with classic analogue 4-20 mA technologies. Using IP as base interaction protocol allows HART-IP to work in the same network together with multiplicity of protocols, based on IP and Ethernet. More than 60 millions devices with HART protocol supporting are installed in the world. HART over Ethernet or HART-IP widen HART accessibility in local internal industrial networks with interconnection with corporate networks and ERP (Enterprise Resource Planning) software. Variables and diagnostic data in HART are encapsulated in HART-IP packets. It allows to realize real time processes in existing corporate networks and to use corporate VPN (Virtual Private Networks).

Figure 1. Viewing HART IP protocol packets in Wireshark network analyzer



During December 2013 – June 2017 European TEMPUS TATU (Trainings in Automation Technologies for Ukraine) project was realized (URL-7, 2018). Within the framework of this project TATU Smart Lab (TSL) equipment was obtained (Gorb et al, 2017a, 2017b). TSL is a flexibly configurable mobile set of devices for teaching modern automation technologies and its application in real projects. It contains devices from different European manufacturers and matches to goals of Industry 4.0, IoT and IIoT concepts (2 hardware modules (HM) of 3) where individual devices and their nodes can

communicate with each other and consumers using wireless data transmission technologies or IP technologies.

The first HM (Fig. 2) contains two programmable controllers (AXC 3050 and ILC 151 GSM/GPRS), PROFINET I/O devices, managed network switch and wireless access point for wireless LAN (Gorb et al, 2017a, 2017b). This HM can be used for studying a wide range of topics including working with data transfer technologies based on Ethernet, wireless data transmission and IP technologies. Two programmable controllers can communicate using TCP/IP or Modbus TCP data transfer protocols. Possible complex industrial IP network structure based on multi interface AXC 3050 smart controller shown at Fig. 3.

Controller EC2250 EtherCAT (Fig. 4), installed in second HM and working with IP-based protocols, has a short cycle time and designed for hard real-time systems [8, 9]. The controller uses a high-performance Cortex A9 800 MHz ARM processor. EtherCAT is an Ethernet based bus standardized by SEMI (Semiconductor Equipment and Materials International), IEC and ISO. EtherCAT is much faster than traditional buses and industrial Ethernet based solutions. The typical EtherCAT cycle time is 50-250 μs, while in traditional buses 5-15 ms are required for each update. The device integrates communication interfaces Ethernet, EtherCAT, CAN, CAN Open, RS232/485, PROFINET, BACnet, Modbus TCP, TCP/IP.

Figure 2. PROFINET hardware module

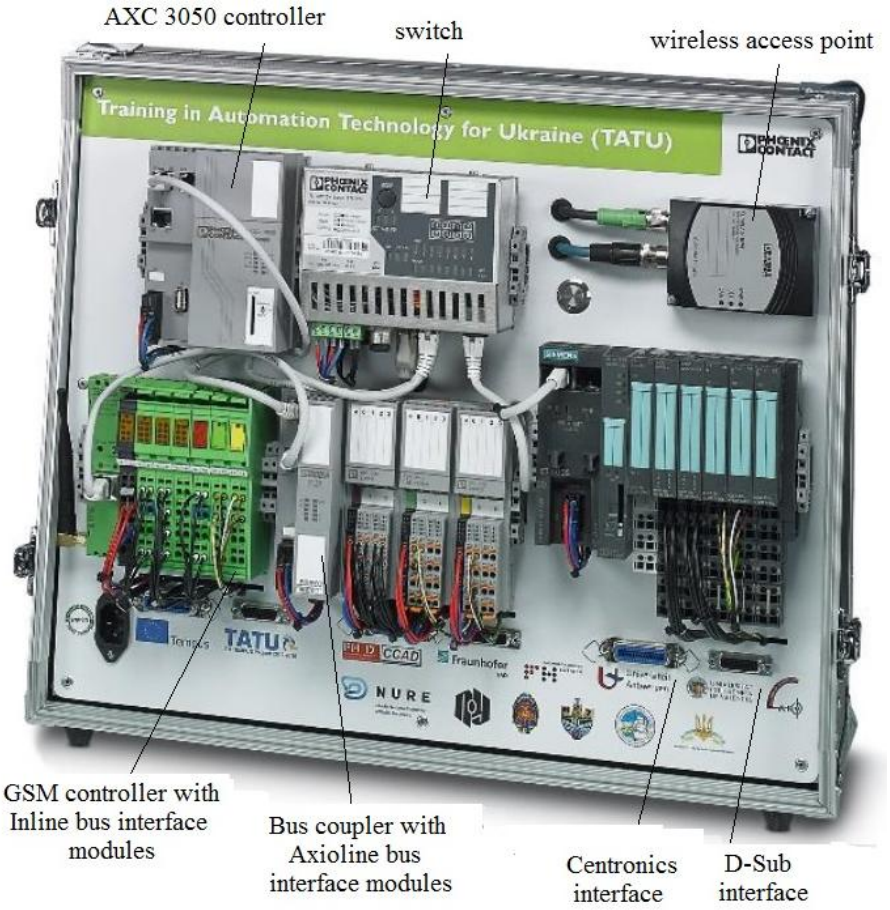


Figure 3. Complex industrial IP network structure based on multi interface controller

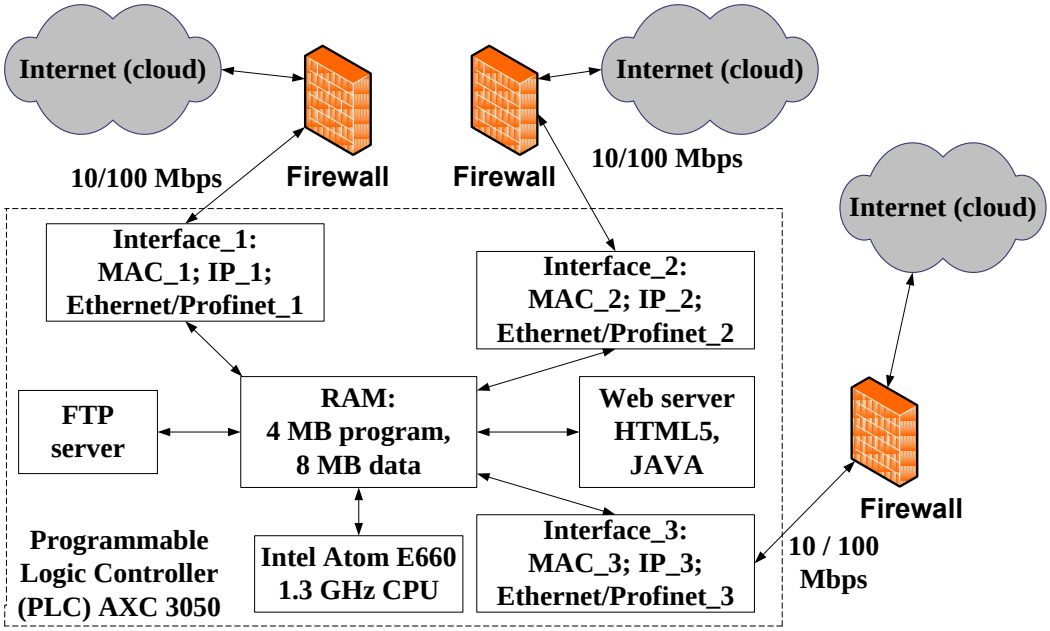
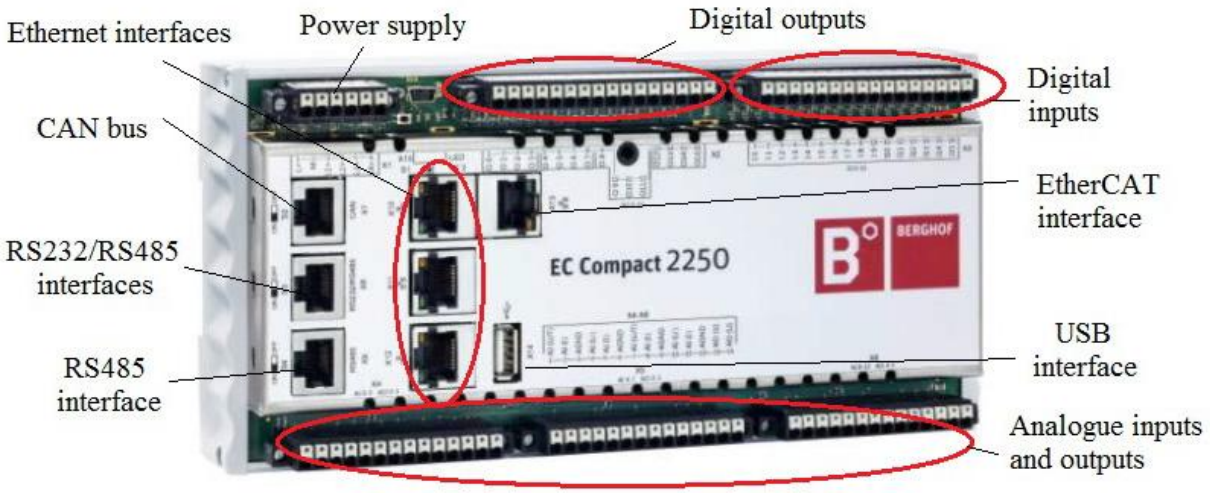
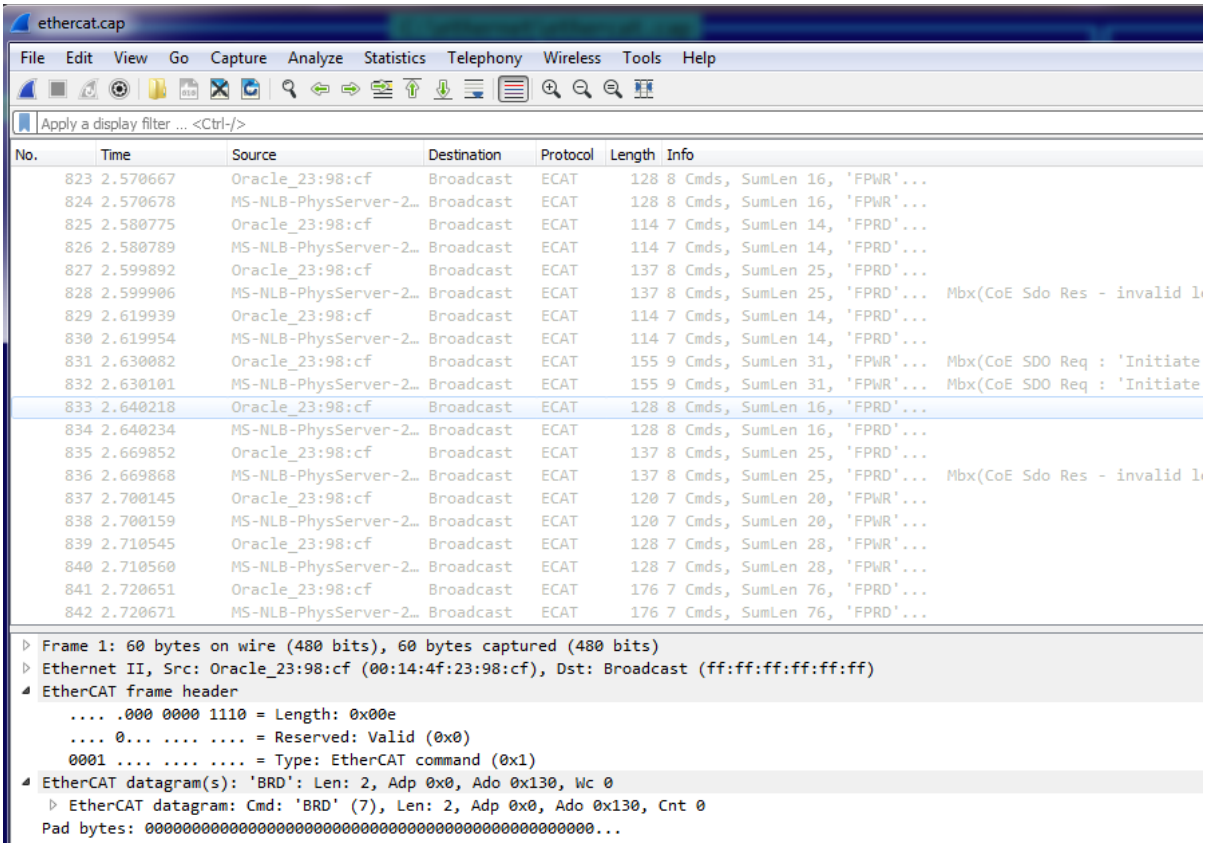


Figure 4. Multi interface industrial IP network controller



WIRESHARK software allows to analyze network traffic in industrial networks based on protocols and technologies described above. Also Wireshark supports capturing of long list of different network protocols. It significantly helps to understand the reason of unobvious network problems, to simplify complex industrial and corporate networks exploitation and making interconnection between different network technologies and protocols using corresponding hardware and software gateways.

Figure 5. Viewing EtherCAT protocol packets in Wireshark network analyzer



3. CONCLUSION

Industrial classic and IP based data transfer protocols and technologies are briefly analyzed. Possibilities of Wireshark network traffic analyzer and examples of industrial networks traffic capturing are shown. Complex industrial IP network structure based on multi interface controller is proposed. Using of equipment, ready for application within the framework of Industry 4.0, IIoT and IoT concepts jointly with Wireshark network traffic analyzer is described.

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THE EFFECT OF HOME VISITS BY NURSES ON THE PHYSICAL AND PSYCHOSOCIAL HEALTH OF THE ELDERLY: STUDY PROTOCOL FOR A SYSTEMATIC REVIEW AND META-ANALYSIS

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ABSTRACT

One of the most significant global demographic tendencies is the rapidly aging world population which will soon be a global health problem. Community health nurses can easily address, observe the risk factors of the elderly's health and health-promoting behaviors during home visits. Home visits reduce the mortality and hospitalization rates of the elderly and enable taking measures against many risky situations. Scientific evidence exists for the fact that more frequent home visits reduce mortality and hospitalization. The objective of systematic review and meta analysis is to identify and synthesize the evidence on the effectiveness of home visits by nurses on the physical and psychosocial health of the elderly.

Systematic review and meta analysis, study design was used. The included studies design of randomized controlled, quasi-experimental and observational (cohort, case-control, cross-sectional), Turkish and English, between December, 2004 and December 2016 (but not finished, ongoing) including a home visit attempt and health outcomes will include physical and psychosocial health. Medline (6860 articles), Web of Sciences (1933 articles), Pubmed (1551 articles), Science Direct (1021 articles), Cinahl Plus with Full Text (1020 articles), Cochrane (501 articles) Tubitak (98 articles), and Yök (126 articles) were searched among a total of 13.110 abstract databases. Scientific evidence exists for the fact that more frequent home visits reduce mortality and hospitalization.The results of this study will help to identify and synthesize the evidence on the effectiveness of home visits by nurses on the health of the elderly.

1. INTRODUCTION

One of the most significant global demographic tendencies is the rapidly aging world population which will soon be a global health problem (WPA, 2015; WPP, 2012). Thanks to the developments in health and socioeconomics, mortality and morbidity rates have fallen in both contagious diseases due to infectious conditions and in non-contagious diseases. When these demographic and epidemiological changes are integrated with rapid urbanism, modernization, globalization, risk factors, and the changes in life styles, chronic cases become increasingly important. Effective strategies are required for health systems in order to expand

health services and meet the needs of elderly individuals aged 65 and above (Chatterji *et al.,* 2015).

Along with the increase in elderly population, inequality in income distribution and insufficient access to health and social support services has increased, causing disease burden and global health risks. These health risks are associated with insufficient access to health services and poverty in most developing countries. For example, the epidemiological profiles are directed by a number of factors such as rapid urbanization, changing nutrition habits, or physical activity; however, valid and effective outcomes are obtained in developed countries (Steptoe *et al.,* 2015; Suzman *et al.,* 2015). The increasing percentage of the elderly population in the total population has brought health, environmental, economic and social problems. Today, mostly women and young girls are responsible for giving care to elderly individuals. Changes in family structure, transition from extended family type to nuclear family type and women's involvement in work life have increased the need of the elderly for institutional care (Tezcan and Seçkiner, 2012).

The success of protective and promotive efforts for elderly health depends on elderly health policies developed considering the needs of elderly individuals. Policies to be developed should be community-based and care-oriented. They should not include medical care alone. Community-based care covers maintaining and promoting health, and providing health and social services for elderly individuals in their own living areas to prevent or delay diseases and disabilities or to minimize their effects (Tarricone and Tsouros, 2008). Methods such as home visits by nurses are required for addressing elderly health problems. Home visits include a series of care at different levels: primary (health education, reduction of the risk, safety, protection and promotion of health), secondary (early diagnosis), and tertiary (adaptation to new conditions and rehabilitation). In addition, these home visits should focus on various subjects such as physical activity, drug compliance and environment (Gillespie *et al.,* 2011).

It is not inevitable for elderly people to suffer in old age due to deteriorated health status or disability. Many elderly individuals want to live as long as possible in their own home, independently and in good health. One reason for this wish is the costs of institutional care in hospitals or nursing homes. Considering their wishes, policy-makers have made it a social and economic priority that elderly people receive care and treatment in their own homes to help protecting them from diseases and disabilities and promoting their health. Elderly people's social and economic difficulties and disability both cause them to feel more independent in their own home. Home visits for elderly individuals can be used to achieve these purposes more easily (Gillespie *et al.,* 2011;Grady,2011; Steptoe *et al.,* 2015; Suzman *et al.,* 2015).

Nurses and scientists working in nursing have always been leaders in elderly care, and they will have a critical role in addressing elderly care problems in the future. They will continue to find scientific evidence to improve clinical care and enhance the quality of life of the aging population (Gillespie *et al.,* 2011). Nurses provide healthcare for elderly individuals in first step health institutions, within the community, in hospitals, in nursing homes and in palliative care centers. Community health nurses can easily address and observe the risk factors of the elderly's health and health-promoting behaviors during home visits (Gillespie *et al.,* 2009).

Home visits reduce the mortality and hospitalization rates of the elderly and enable taking measures against many risky situations such as falling. Based on the studies analyzing the lifelong costs of nursing homes, home visits with frequent follow-ups are recommended

for each individual older than 40 years old (Stuck *et al.,* 2002). Home visits can yield more cost-effective outcomes compared to long-term institutional care (Chatterji *etl al.,* 2015; Steptoe *et al.,* 2015; Stuck *et al.,* 2002). Scientific evidence exists for the fact that more frequent home visits reduce mortality and hospitalization, particularly for younger elderly individuals (aged 60). However, studies analyzing the effectiveness of home visit programs for elderly people may have conflicting results (Gillespie *et al.,* 2009; Stuck *et al.,* 2002; Van Haastregt *et al.,* 2000).

Researchers have reported that a single study cannot be adequate when conflicting results are seen in the solution of a problem and recommended that the results of independent studies on the same subject be synthesized (Borenstein *et al.,* 2009; Hadich, 2010). These studies consist of meta-analyses providing high-level evidence on the effective use of time and costs. This method assesses the inconsistencies in the literature and analyzes their causes, increasing the estimation power of the studies, obtaining cost-effective results and introducing new approaches that can be analyzed in subsequent studies (Haidich, 2010).

In conclusion, cost-effective (low cost) solutions should be developed to improve the functional conditions of elderly people and increase the effectiveness of interventions (Chatterji *et al.,* 2015). One of the best ways to protect and promote the physical and psychosocial health of elderly individuals and provide them with health service is regular home visits. Individuals' needs for health and care increase in old ages. Community health nurses who provide care for elderly individuals in their own environment increase the quality of life of elderly individuals and their families and provide them with healthcare based on clinical care, education and counseling through home visits. Although this subject has such importance, no meta-analysis studies were found to have been conducted on the effect of home visits by nurses on the physical and psychosocial health of elderly individuals in the last 20 years. Studies should be conducted on the effect of home visits by nurses on the physical and psychosocial health of elderly people. PICOS (participants, interventions, comparisons, outcomes, and study design) used in describing the problem. The objective of this quantitative systematic review and meta analysis is to identify and synthesize the evidence on the effectiveness of home visits by nurses on the physical and psychosocial health of the elderly. The proposed review will aim to address the following questions:

1. What is the effect size of home visits regarding the physical and psychosocial health of the elderly?
2. What is the effect size of the health outcomes of home visits regarding the physical and psychosocial health of the elderly according to gender? Is gender a moderator variable?
3. What is the effect size of the health outcomes of home visits regarding the physical and psychosocial health of the elderly according to country of residence? Is country of residence a moderator variable?
4. What is the effect size of the health outcomes of home visits regarding the physical and psychosocial health of the elderly according to the unit they receive home care services?
5. What is the effect size of the health outcomes of home visits regarding the physical and psychosocial health of the elderly according to the duration and frequency of the visits? Are the duration and frequency of the visits moderator variables?
6. What is the effect size of the health outcomes of home visits regarding the physical and psychosocial health of the elderly according to the status of receiving home based care? Is the status of receiving home based care a moderator variable?

7. What is the effect size of the health outcomes of home visits regarding the physical and psychosocial health of the elderly according to whether or not using model? Is whether or not using model a moderator variable?
8. What is the effect size of the health outcomes of home visits regarding the physical and psychosocial health of the elderly according to the elderly population studied (general population, those with health problems)?

2. MATERIAL AND METHODS

2.1. Design and methods

The study carried out August 2016 and May 2017.

2.2. Types of participants

1. English and Turkish studies (articles, investigation reports and dissertations) published in refereed and non-refereed journals as well as electronic journals between December, 2004 and December, 2016.

2. Published or unpublished study resources: Master's and PhD theses

3. Studies with appropriate research method [randomized controlled studies, quasi-experimental studies and observational studies (cohort, case-control, cross-sectional)].

4. Studies with sufficient numeric data for analysis (Pearson's correlation coefficients, chi-square values and t-, p, sample size (N), F-values, etc. or calculability of these values)

5. Studies including a home visit attempt (practice, intervention, life satisfaction, etc.) to promote the physical (nutrition, hypertension, physical activity, cancer, stroke, pain, falling, sleep, etc.) or psychosocial (dementia, depression, quality of life, social support, loneliness, social isolation, anxiety, life satisfaction, etc.) health of the elderly

6. Studies in which the intervention is carried out by home visits (at least one step of the intervention)

7. Home-based practices performed via home visits,

8. Home visits are carried out by nurses, or nurses direct those carrying out the home visits,

9. The studies design of randomized controlled, quasi-experimental and observational (cohort, case-control, cross-sectional)

10. Quantative studies having received a "moderate" or "strong" score on the quality assessment tool.

2.3. Types of interventions

This systematic review and meta analysis will consider studies that effect of home visit interventions by nurses on the elderly health. Health outcomes will include physical (nutrition, hypertension, physical activity, cancer, stroke, pain, falling, sleep, etc.) and psychosocial (dementia, depression, quality of life, social support, loneliness, social isolation, anxiety, life satisfaction, etc.) health. Interventions may include face-to-face delivery, group delivery or any other relevant method or combination of methods in participants' homes.The interventions may involve one or more sessions and can also vary in duration. It is carried out by home visits, or home-based practices performed via home visits. A nurse is a person who is legally licensed and/or registered to practice the full scope of nursing in his or her country.

2.4. Types of outcomes

Primary outcomes: quality of life, social support, life satisfaction, mortality, falling, depression, management of hypertension, pain, social isolation Secondary outcomes: Self-Reported perceived health, emergency department visits, length of hospital stay.

2.5. Types of studies

The randomized controlled studies, quasi-experimental studies and observational studies (cohort, case-control, cross-sectional).

Exclusion criteria

1. Studies written in other languages than Turkish and English
2. Visits carried out by another health professional than nurses
3. Studies including insufficient numeric data for analysis
4. Duplicates: for the studies published in more than one paper, the paper with largest sample size will be included.
5. Studies whose full data will not be accessible even after requested from the authors.
6. Studies having received a poor score on the quality assessment tool

2.6. Search strategy

Search Process (keywords)

Meta analysis, home visits, (in-home visiting, domiciliary visits), nursing, elderly health, community health nursing, health visitors, visiting nurses, physical health, psychosocial health, old people, aged, elderly people, elders, seniors, intervention, effect, etc. and various combinations of their Turkish equivalents were used during the search. We were benefited MeSH (Medical Subject Headings) terms for selection of key words. Medline (6860 articles), Web of Sciences (1933 articles), Pubmed (1551 articles), Science Direct (1021 articles), Cinahl Plus with Full Text (1020 articles), Cochrane (501 articles) Tubitak (98 articles), and Yök (126 articles) were searched among a total of 13.110 abstract databases. This search was completed in six months. The search was limited to the studies conducted on home visits by nurses in the last 11 years (between December, 2004 and December, 2016), conducted in Turkish and English, and conducted only with the elderly population. However, advance search will continue until the end of the study.

The first stage of this systematic review will involve the evaluation of titles, abstracts and eligibility of studies. In the second stage, full text of the papers will be independently assessed by two independent observers to confirm their eligibility. Bibliographic details of the studies will be downloaded or manually entered into the EndNote X747 references management database. The search for ongoing clinical trials will be performed in the following databases: www. controlled - trials. com; www. clinical trials. com; www.who.int/trialsearch. Manuel searches will be conducted in key journals. Government reports, theses and dissertations and their references lists.

2.7.Assessment of methodological quality

Quality assessments (risk of bias assessments) will be conducted by two independent reviewers for each study included. The Quality Assessment Tool for Quantitative Studies, developed by academic members in master's program within the scope of the Effective Public Health Practice Project (EPHPP) will be used for quality assessment. It is a valid and reliable tool (Thomas *et al.*, 2004). This tool consists of eight sections: bias of selection, study design, confounder, blinding, data collection method, exclusion from and withdrawal from the study, integrity of intervention, and analysis. Except for integrity of intervention and analysis, each section is scored as 1=Strong, 2=Moderate, and 3=Poor. After each section is scored, the study is given a general score based on the dictionary. Having no Poor scores indicates a methodologically strong study, one Poor score indicates a study with moderate reliability, and two or more Poor scores indicates a methodologically unreliable study. Based on the assessment and scoring, each assessor expresses their final decision as 1=Strong, 2=Moderate,

and 3=Poor. After scoring, any inconsistencies between the assessors are examined along with the reasons for any inconsistency. No scores are given for intervention integrity and analysis. These sections guide the assessors when they have hesitation about the quality of the study, as well as contributing to the Discussion section of this study. The formation of the Turkish version and validity reliability study have been conducted by researchers. Permission has been obtained from the relevant institution for its use. The validity and reliability tests are conducted for its Turkish adaptation. The expert evaluation showed a content validity index was 0.99. The opinions of eight experts were evaluated using Kendall W analysis, which revealed that there was no statistical difference (Kendall W = 0.13, p = 0.319) among their opinions and that their scores were consistent with each other. It is a reliable tool that can be used to assess the quality of quantitative studies.

This protocol adheres to PRISMA-P standards for protocol reporting. And we are using flow diagram. We shall conduct a systematic review and meta-analysis and we will report the outcomes according to the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) statement The PRISMA-P checklist contains 17 items considered to be essential and minimum components of a systematic review or meta-analysis protocol (Moher *et al.*, 2009).

This protocol was registered with the International Prospective Register of Systematic Reviews (PROSPERO) on 05-0-2017. PROSPERO 2017: CRD42017054228 Available https://www.crd.york.ac.uk/PROSPERO/display_record.asp?ID=CRD42017054228. This study is supported by Selçuk University Scientific Research Projects Coordinator (Project No: 15102040). And approval was obtained from the Ethics Committee of Selcuk University.

2.8.Data extraction

The study titles and abstracts will be screened by two authors in the review group independently to identify eligible studies. The articles selected by two independent observers will be compared and a consensus will be made by discussing on the different ideas regarding an article. Two independent observers who have worked on research and elderly health will ensure the reliability of the coding. The study coding protocol including study number, title, authors, year of the study, country of the study, publication type, status of being published, content, objectives, status of receiving institutional services, elderly population studied, status of whether or not using model, the frequency and duration of the visits, study design, sample size, dependent and independent variables analyzed in the study, calculated measures and statistical methods will be used for coding. Inter-coders reliability will be sought by Kappa analysis.

2.9. Data synthesis

The methods appropriate for the data type among the methods of integrating the study results will be selected for data analysis. Analyses will be performed using the Comprehensive Meta-Analysis (CMA) version 3 program to apply the meta analysis technique. The studies will be assessed for statistical heterogeneity considering the settings, populations, interventions and outcomes. The statistical heterogeneity of the combined studies will be tested using the I-squared, which describes the percentage of total variation across a study due to heterogeneity rather than chance. Publication bias will also be assessed using a funnel plot, Orwin's failsafe N test, and Duval and Tweedie's trim and fill tests.

3. RESULTS

Data collection is ongoing. At the same time 13.110 abstract were screened. Quality assessment is continuing.

4. DISCUSSION AND CONCLUSION

Scientific evidence exists for the fact that more frequent home visits reduce mortality and hospitalization. However, studies analyzing the effectiveness of home visit programs for elderly people may have conflicting results. Researchers have reported that a single study cannot be adequate when conflicting results are seen in the solution of a problem and recommended that the results of independent studies on the same subject be synthesized. Systematics reviews and meta analysis will provide the highest level of informed decisions. Despite there are many meta-analyzes in this issue, there are no data that it had been in the last 20 year and so comprehensive in the literature. But one limitation of this study is that the studies conducted on home visits by nurses in the last 11 years (between December, 2004 and December, 2016), conducted in Turkish and English, and conducted only with the elderly population. But we hope that it will lead to future works.

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Ethics

Study was approved by the Ethics Committee of Selcuk University (ECSU), ECSU No: 2015/48, 30.06.2015.

Conflicts of interest

Authors declare that there are no conflicts of interest.

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HISTOPATHOLOGICAL CHANGES IN THE STOMACH MUCOSA OF RATS FED WITH GREAT SCALLOP (Pecten maximus)

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ABSTRACT

Heavy metals, industrial and household wastes and pesticides are threats for the aquatic ecosystem. Polluted water sources are streaming into the seas and cause pollution in these systems. Dardanelles is exposed to pollution from the Marmara and Black Sea. Our previous studies demonstrated that the water and mollusc from certain regions of the Dardanelles contained heavy metal salts. The purpose of the study is to demonstrate the histopathologic changes in the gastric tissues of rats which are fed with great scallop (Pecten maximus) that are collected from the Çardak region of the Dardanelles. Four groups of rats are included in the study, group 1 (n=6), control group fed with standard rat food, group 2 (n=6), 75% great scallop and 25% standard rat food daily, group 3 (n=6), 75% great scallop and 25% standard rat food every two days, group 4 (n=6), 75% great scallop and 25% standard rat food every three days. After the routine histopathologic processing all gastric tissue samples are evaluated in terms of 8-hydroxy-2' -deoxyguanosine (8-OHdG) immunoreactivity with light microscopy and image analysis software. No histopathologic differences found in standard hematoxylin-eosin (H.E.) stained gastric tissue samples of the control group. Second group showed active chronic gastritis, third group showed less inflamation and chronic gastritis compared with the second group and fourth group showed less mononuclear inflammation compared to the second and third groups. In immunohistochemical staining, 8-OHdG immunoreactivity in gastric epithelial cells. 8-OHdG immunoreactivity was negative in stomach tissues in all groups. There was no statistically significant difference between the groups that were fed every day, every other day and every three days with great scallop (p>0.05). The results of our studies showed that rats fed more with great scallops could produce gastritis in the stomach.

1. INTRODUCTION

Sea pollution is an indispensable part of environmental pollution. Domestic and industrial wastes, nuclear power stations built for electric generation, erosions, improper coastal fill areas, oil pollution, and marine accidents are significant factors causing sea pollution (Topcuoğlu et al., 2003; Tüzen 2003).

Aerobic organisms possess antioxidant defense systems that deal with reactive oxygen species (ROS) produced as a consequence of aerobic respiration and substrate oxidation.

Small amounts of ROS, including hydroxyl radicals (OH), superoxide anions (O_2) and hydrogen peroxide (H_2O_2), are constantly generated in aerobic organisms in response to both external and internal stimuli (Hurst et al 1997; Jornot et al., 1998) . Low levels of ROS are indispensable in many biochemical processes, including intracellular messaging in the cell differentiation and cell progression or the arrest of growth, apoptosis (Ghosh et all. 1998), immunity (Yin et all. 1995) and defense against micro-organisms (Bae et all. 1997; Lee et all. 1998). In contrast, high doses and/or inadequate removal of ROS result in oxidative stress, which may cause severe metabolic malfunctions and damage to biological macromolecules (Chopra et all., 1998; Czene et all., 1997; Wojtaszek 1997).

Under normal conditions, the proportion of heavy metals in the environment is low. When the concentration ratio in the natural environment increases, heavy metals such as silver, mercury copper, cadmium and lead are toxic on organisms and inhibit enzymes. For some enzymatic activities in the living world, certain metals are necessary, provided they are in certain concentrations. The metals bound to the organic material can be used during biological activities and dissolve again by dissociation of the organic materials (Balkıs et all., 2005). Estimates of intake of these elements were made through seafood consumption by the general population Turkish legal standards, are 1.0 ppm for Cd and 2.0 ppm for Pb in bivalve molluscs (Anonymous 2000).

Heavy metals were detected in seawater and many molluscan species that growing in the Dardanelles (Gezen et all., 2011; Demir et all., 2011; Gezen et all., 2011; Özkurnaz et all., 2012). The accumulation of heavy metals have investigated in the carpet shell clams, great scallops, sea snails and oysters from the Dardanelles Umurbey region. In this research, Zn in carpet shell clams, Zn and Mn in great scallops, Zn in oysters, Al, Zn, Fe, Cu and Mn in sea snails found the metals as high. If the same zone is in seawater, the Zn level is high (Gezen et all., 2011). In sea chestnuts growing in Dardanells, the values of Al, Zn, and Fe in samples taken from Gelibolu Hamzakoy station are high. Al and Fe values were higher in samples taken from Çardak region. Al, Fe and Zn values were higher in samples taken from Umurbey region. Al, Fe and Zn values were higher in samples taken from Çamburnu region (Gezen et all., 2011). The accumulation of heavy metals have investigated in the carpet shell clams, great scallops, sea snails and oysters from the Dardanelles Karacaören region. In this research, Al, Zn and Fe in carpet shell clams, Zn and Mn in great scallops, Zn in oysters, Al, Zn, Fe, Cu and Mn in sea snails found the metals as high (Demir et all., 2011).

There is no research revealing histopathologic changes in the stomach tissues of living beings fed with great scallops collected from the Çardak region (Çanakkale, Turkey). The purpose of the study is to demonstrate DNA damage and the histopathologic changes in the gastric tissues of rats which are fed with great scallops that are collected from the Çardak region (Çanakkale, Turkey).

2. MATERIAL AND METHODS

2.1. Ethics Statement

The study protocol was approved by the Çanakkale Onsekiz Mart University Ethics Committee for Animal Research (Protocol number: 2010/09-03).

2.2. Animal Model

A total of 24 male Wistar albino rats, weighing 290–310 g, were used in the study. The rats were kept for 30 days under appropriate conditions of temperature/humidity and a 12-h light cycle while being provided sufficient water and feed. The rats were randomly selected and divided into 4 groups. For the first study group (n: 6), was the control group; standard rat diet was given every days. For the second study group (n: 6), 75% great scallop +

25% standard rat diet standard rat feeds were given daily. For the third study group (n: 6), 75% great scallop + 25% standard rat diet was given every two days. Standard rat diet was given the other day. For the fourth group (n: 6), 75% great scallop + 25% standard rat diet was given every three days. Standard rat diet was given the other two day.

Rats were fed twice daily for 30 days at 15% of their weight every morning and evening at the same time. The great scallop given as food to the rats were removed from the Dardanelles Çardak region (Figure 1). Average 40-60 g weight were selected. After the beaks were overcooked, the meat broke off and the meat at 100 degrees was dried.

Figure 1: *Dardanelles Çardak region (Çanakkale, Turkey).* ***Arrow****: The area where the great scallops are collected.*

It was weighed into each rat's weight and 10 mg/kg intraperitoenal ketamine hydrochloride (Ketalar, Eczacibasi, Istanbul, Turkey), and 20 mg/kg of xylazine 2% (Rompun, Bayer Turkey Pharmaceutical Ltd., Istanbul, Turkey) were anesthetized. The rats were anesthetized and then sacrificed.

2.3. Histological evaluation

The stomach tissues were maintained in immunofix (Leica) for 24 hours for histopathological examination. The paraffin embedded stomach tissues were stained with hematoxylin and eosin (H & E) at a thickness of 5 microns. Immunohistochemical staining method was applied by cutting the paraffin embedded stomach tissues 3 microns in thickness.

The LAB-SA Detection System, (Histostain-Plus Bulk Kit, Invitrogen) was applied to determine immunohistochemical localization of 8-hydroxydeoxyguanosine (8-OHdG) in tissues. Slides were incubated with polyclonal goat anti-8-Hydroxydeoxyguanosine (8-OHdG, Millipore Corporation) antibody, which was diluted 1:200 for the stomach tissue, for 30 minute at room temperature. Diaminobenzidine-tetra hydrochloride (DAB, Invitrogen Corporation) was used as the colorant. Also Mayer's hematoxylin stain was used as a nuclear counterstain.

Dye samples were evaluated on the Zeiss AXIO Scope 1 brand research microscope. Analysis of 8-OHdG immunoreactive cells in the stomach tissue was performed using the Leica LAS V3.8 image analysis system. Five of the sections from the blocks containing the stomach tissues of all the rats in all groups were stained. From the stained sections, 1000 cells were counted and immunoreactive cells were identified among these cells. Tosun et all., (2006); Bakır et all., (1996); Avunduk et all., (2000) for this purpose;

Immunopositive cells / Total cell count (1000) --------- x 100 % = ….. % formula were used .

2.4. Statistical analysis

SPSS 15 version was applied for the statistical evaluation of the results obtained with the applied formula. Kruskal-Wallis Test was used for nonparametric tests to determine the differences between survivin immunoreactivity groups. The difference between the groups was considered significant in the results of $p < 0.05$.

3. RESULTS

There was no significant change in the staining of the stomach of the rats in the first group with Hematoxylin Eosin (Figure 2).

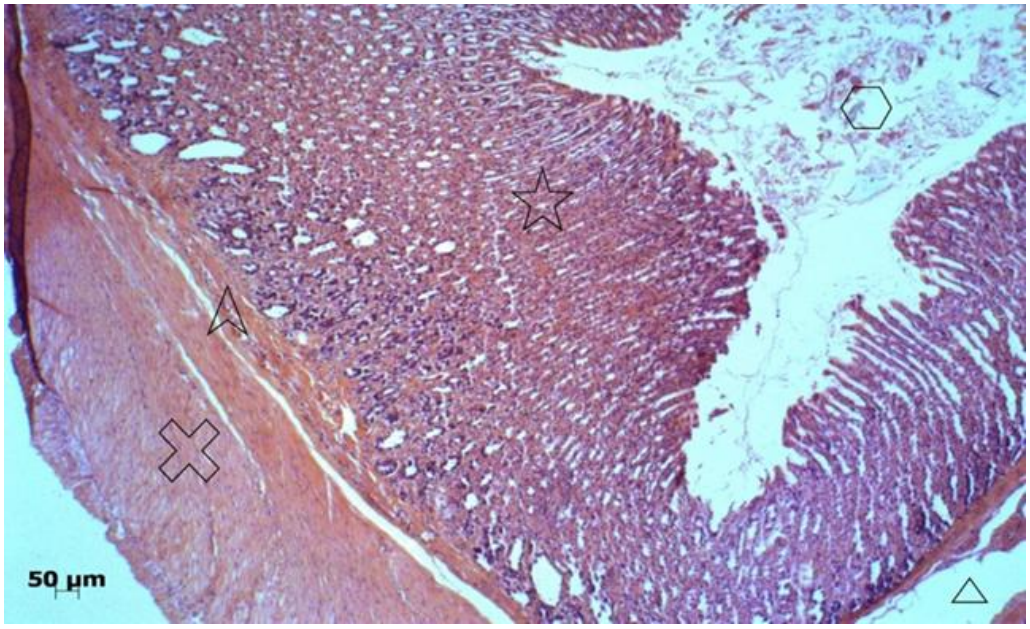

Figure 2. For the first study group was the control group; standard rat diet was given every days. Rat stomach, (H.E.x5). **Star:** Lamina propria mucosa; **Pointed arrow:** Lamina muscularis mucosa; **Arrow head:** Lamina submucosa; **Crossed:** Tunica muscularis; **Hexagon:** Gastric lumen.

In the second group, there were active chronic gastritis findings in the rat gastric mucosa (Figure 3). Mononuclear inflammatory cells were observed as foci between the lamina propria and the border of the lamina muscularis. Besides, common mononuclear cells were detected in lamina propria mucosa, lamina muscularis mucosa and lamina submucosa.

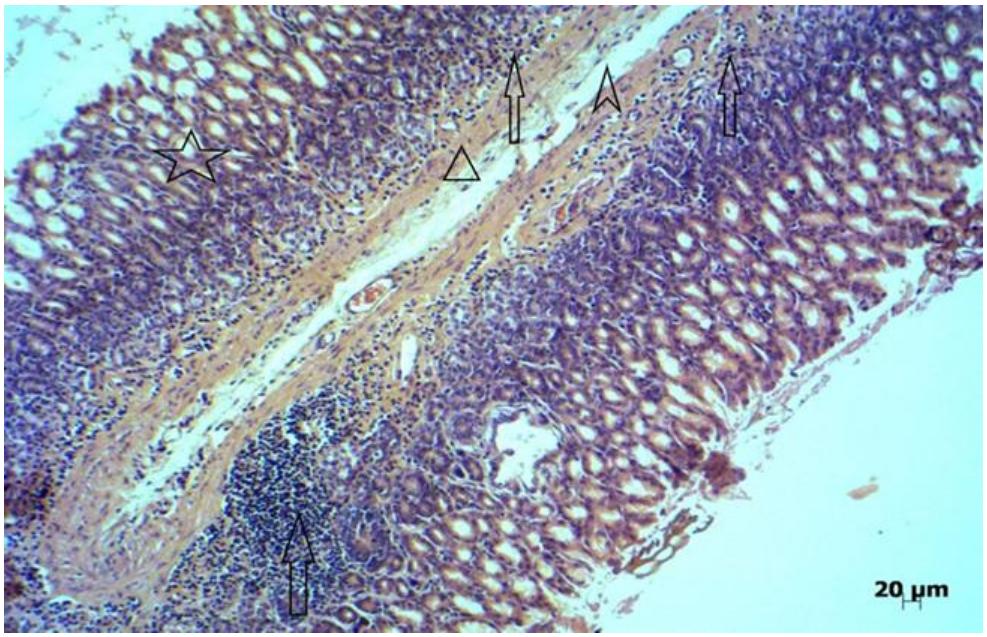

Figure 3. For the second study group; 75% great scallops + 25% standard rat diet standard rat feeds were given daily. Rat stomach, (H.E.x10). **Star:** Lamina propria mucosa; **Arrow head:** Lamina muscularis mucosa; **Pointed arrow:** Lamina submucosa; **Arrows:** Mononuclear inflammatory cells

In the third group, mononuclear inflammatory cells were observed in some areas of the lamina muscularis mucosa, more in the lamina propria mucosa (Figure 4).

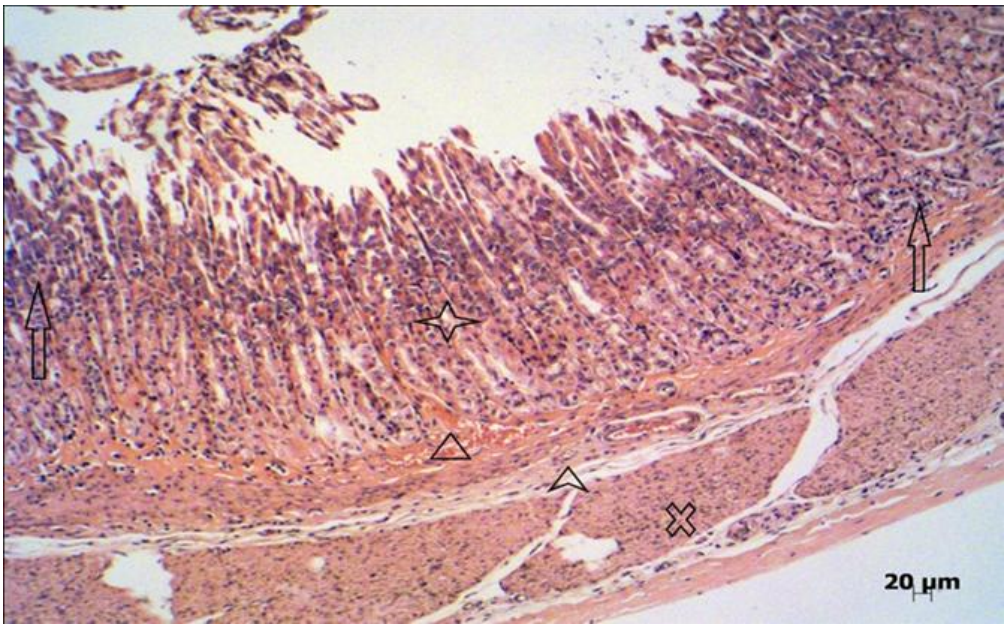

Figure 4. For the third study group; 75% great scallops + 25% standard rat diet was given every two days. Standard rat diet was given the other day. Rat stomach, (H.E.x10). **Star:** Lamina propria mucosa; **Arrow head:** Lamina muscularis mucosa; **Pointed arrow:** Lamina submucosa; **Crossed:** Tunica mucosa; **Arrow:** Mononuclear inflammatory cells.

In the fourth group, mononuclear inflammatory cells were rarely seen in some areas of the lamina muscularis mucosa, more in the lamina propria mucosa (Figure 5).

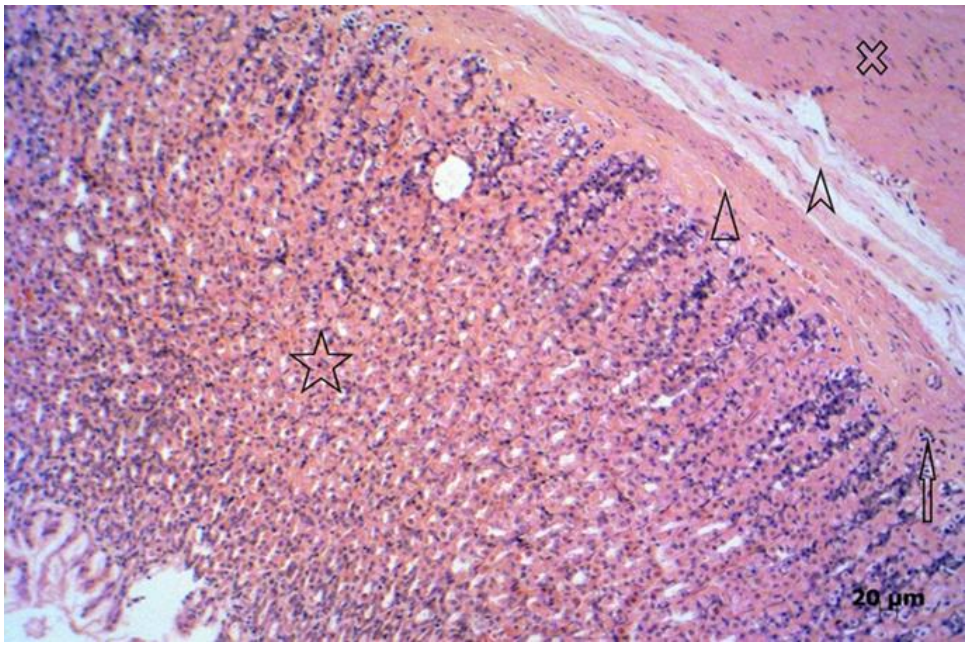

Figure 5. For the fourth group; 75% great scallops + 25% standard rat diet was given every three days. Standard rat diet was given the other two day. Rat stomach, (H.E.x10). **Star:** Lamina propria mucosa; **Arrow head:** Lamina muscularis mucosa; **Pointed arrow:** Lamina submucosa; **Crossed:** Tunica muscularis: **Arrows:** Mononuclear inflammatory cells

8-OHdG immunoreactivity was negative in stomach tissues in all groups. No significant differences were detected between groups in immunohistochemical staining with 8-OHdG (Figure 6).

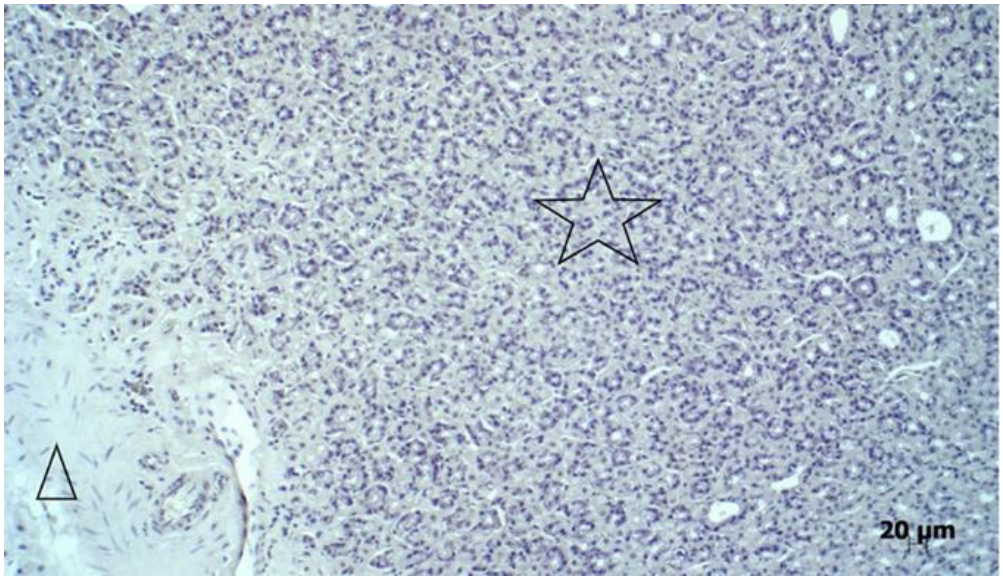

Figure 6. For the second study group; 75% great scallops + 25% standard rat diet standard rat feeds were given daily. Rat stomach. (8-OHdGx10). **Star:** Lamina propria; **Arrow head:** Lamina muscularis.

4. DISCUSSION

Extensive mononuclear cell infiltration was detected in the stomach of all rats consuming great scallops every day for 30 days, especially in the lamina propria mucosa, with foci of mononuclear inflammation and in all mucosa layers. Extensive mononuclear cell infiltration was detected in tunica mucosa layers of gastric tissue of rats consuming great scallops every other day for 30 days. Mononuclear cell infiltration was detected in the tunica mucosa layers of the stomach of the rats consuming mussels every three days for 30 days.

Cadmium, which is a highly toxic metal, causes necrosis by accumulating especially in liver and kidney (Kara et all., 2004). It has been revealed that heavy metals can cause chronic degenerative changes and, in some cases, can cause teratogenic and carcinogenic effects, especially by affecting the nervous system, liver and kidneys (IARC 1987). In addition to the findings of other researchers, we have also found that heavy metal salts cause histopathological changes in the stomach tissue.

Long-term exposure to heavy metals such as mercury (Hg), lead (Pb), chromium (Cr), cadmium (Cd), arsenic (As), copper (Cu), vanadium (V), nickel (Ni) chronic inflammation, cardiac, pulmonary and neurological effects and some cancers (Nieboer et all., 2013; Mantovani et all., 2008; Clarkson, 2002). In this study, we found mononuclear inflammatory cell growth and chronic gastritis in gastric mucosa of rats fed with great scallops. Findings by some investigators that heavy metals may cause inflammation support our findings.

Some researchers have found that heavy metal salts can cause DNA damage (Fraga et all., 1990; Halliwell et all., 2000; William et all., 2000; Ateş et all., 2004; Burçak et all., 2004; Siomek et all., 2006). Immunohistochemical staining methods are used to detect damage to cells and tissues (Gezen 2017). 8-OHdG was found to be negative in the gastric mucosa of all groups in our study. We could not detect DNA damage in the stomach tissue of rats fed with great scallops. It is thought that heavy metals in low levels (NOEL) in the grains do not cause DNA damage.

However, increased inflammation in the stomach mucosa suggests that digestive system diseases have arisen. The authors think that care must be taken while consuming this kind of great scallops.

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Footness

* At the time of this research, she was working at Department of Pathology of Çanakkale Onsekiz Mart University.

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HISTOPATHOLOGICAL CHANGES IN THE STOMACH MUCOSA OF RATS FED WITH CARPET SHELL CLAM (Ruditapes decussatus)[*]

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ABSTRACT

Free radicals are produced in cells by cellular metabolism and exogenous agents. These specie reacts with biomolecules in cells, including DNA, proteins, lipids and carbonhydrates. The resulting oxidative damage to DNA, is implicated in mutagenesis, carcinogenesis, and aging. Heavy metals, industrial and household wastes and pesticides are threats for the aquatic ecosystem. Polluted water sources are streaming into the seas and cause pollution in these systems. Dardanelles is exposed to pollution from the Marmara and Black Sea. Our previous studies demonstrated that the water and mollusc from certain regions of the Dardanelles contained heavy metal salts. The purpose of the study is to demonstrate DNA damage and the histopathologic changes in the gastric tissues of rats which are fed with carpet shell clam that are collected from the Çardak Lagoon (Çanakkale, Turkey). Four groups of rats are included in the study, group 1 (n=6), control group fed with standard rat food, group 2 (n=6), 75% carpet shell clam and 25% standard rat food daily, group 3 (n=6), 75% carpet shell clam and 25% standard rat food every two days, group 4 (n=6), 75% carpet shell clam and 25% standard rat food every three days. After the routine histopathologic processing all gastric tissue samples are evaluated in terms of 8-hydroxy-2' -deoxyguanosine (8-OHdG) immunoreactivity with light microscopy and image analysis software. No histopathologic differences found in standard hematoxylin-eosin stained gastric tissue samples of the control group. Mucosal specimens of the second, third and fourth groups showed mild mononuclear inflammation in favor of chronic gastritis. In immunohistochemical staining, 8-OHdG immunoreactivity in gastric epithelial cells. 8-OHdG immunoreactivity was negative in stomach tissues in all groups. There was no statistically significant difference between the groups that were fed every day, every other day and every three days with clam ($p>0.05$). The results of our studies showed that rats fed more with carpet shell clam could produce gastritis in the stomach.

[*] This study is the revised version of the same name paper presented in the "2nd International Rating Academy Congress: Hope" held in Kepez / Çanakkale on April 19-21, 2018

1. INTRODUCTION

Free radicals are highly active chemical products that occur in the body during metabolism. The most important free radicals in biological systems are the radicals formed by oxygen (Gulbahar, 2007). Free radicals occur in cells due to endogenous and exogenous sources. Environmental factors such as stress, viruses, infection, exposure to chemicals such as paracuat and alloxan, drug toxications such as pesticides, carbon tetrachloride, paracetamol, ionizing and ultraviolet radiation, air pollutant phytochemicals, cigarette smoke, solvents, cisplatin, antimicrobial agents such as nitrofurantoin, bleomycin, doxorubicin and adriamycin, hyperbaric oxygen, tricyclic antidepressants, metal ions such as iron, copper, cadmium, nickel, chromium and mercury, asbestos fibers, mineral powders, ozone, carbon monoxide, silica, aflatoxin B1 and polychlorinated biphenyl (Fraga et al. 1990; Halliwell, 2000; Williams et al. 2000; Ateş et al. 2004; Burçak et al. 2004; Siomek et al. 2006).

Mechanism of Occurrence of Oxidative Strase-Associated DNA Damage DNA Damage and Causes All changes that occur due to the effects of endogenous or exogenous factors on the molecular integrity of genetic material are called DNA damage. The integrity of genomic DNA is constantly threatened by environmental factors. Changes in DNA structure may occur endogenously during cellular events such as DNA replication and DNA recombination (Kulaksız et al. 2007). DNA damage is a phenomenon that is common throughout the life of the cell and can lead to mutation, cancer, aging, and ultimately cell death. DNA is constantly exposed to changes by cellular metabolites (ROS) and exogenous agents throughout life. These changes can eventually lead to cellular death in single-celled organisms or degeneration and aging in multicellular organisms (Sancar et al. 2004).

We have identified heavy metals in seawater and many molluscan species that growing in the Dardanelles (Gezen et al. 2011; Gezen et al. 2011; Demir et al. 2011; Özkurnaz et al. 2012). In our previous research have investigated the accumulation of heavy metals in the carpet shell clam, great scallops, sea snails and oysters from the Dardanelles Umurbey region. In this research, Zn in carpet shell clams, Zn and Mn in great scallops, Zn in oysters, Al, Zn, Fe, Cu and Mn in sea snails found the metals as high. If the same zone is in seawater, the Zn level is high. In sea chestnuts growing in Dardanells, the values of Al, Zn, and Fe in samples taken from Gelibolu Hamzakoy station are high. Al and Fe values were higher in samples taken from Çardak region. Al, Fe and Zn values were higher in samples taken from Umurbey region. Al, Fe and Zn values were higher in samples taken from Çamburnu region (Gezen et al. 2011). In our previous research have investigated the accumulation of heavy metals in the carpet shell clam, great scallops, sea snails and oysters from the Dardanelles Karacaören region. In this research, Al, Zn and Fe in carpet shell clams, Zn and Mn in great scallops, Zn in oysters, Al, Zn, Fe, Cu and Mn in sea snails found the metals as high (Gezen et al. 2011; Demir et al. 2011; Özkurnaz et all. 2012).

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The study protocol was approved by the Çanakkale Onsekiz Mart University Ethics Committee for Animal Research (Protocol number: 2010/09-03).

2.2. Animal Model

A total of 24 male Wistar albino rats, weighing 290–310 g, were used in the study. The rats were kept for 30 days under appropriate conditions of temperature/humidity and a 12-h light cycle while being provided sufficient water and feed. The rats were randomly selected and divided into 4 groups. For the first study group (n: 6), was the control group; standard rat diet was given every days. For the second study group (n: 6), 75% carpet shell clam + 25% standard rat diet standard rat feeds were given daily. For the third study group (n: 6), 75% carpet shell clam + 25% standard rat diet was given every two days. Standard rat diet was given the other day. For the fourth group (n: 6), 75% carpet shell clam + 25% standard rat diet was given every three days. Standard rat diet was given the other two day.

Rats were fed twice daily for 30 days at 15% of their weight every morning and evening at the same time. The carpet shell clam given as food to the rats were removed from the Çardak Lagoon (Çanakkale, Turkey), (Figure 1). Average 30 ± 10 g weight were selected. After the beaks were overcooked, the meat broke off and the meat at 100 degrees was dried.

Figure 1. The area where the carpet shell clam are collected. **Star**: Çardak Lagoon (Çanakkale, Turkey); **Crossed:** Dardanelles

It was weighed into each rat's weight and 10 mg/kg intraperitoenal ketamine, and 20 mg/kg of xylazine 2% were anesthetized. The rats were anesthetized and then sacrificed. After the rats have received the stomachs other organs were also taken for further research.

2.3. Histological evaluation

The stomach tissues were maintained in immunofix (Leica) for 24 hours for histopathological examination. The paraffin embedded stomach tissues were stained with hematoxylin and eosin (H & E) at a thickness of 5 microns. Immunohistochemical staining method was applied by cutting the paraffin embedded stomach tissues 3 microns in thickness. For 8-hydroxydeoxyguanosine (8-OHdG) staining, tissue samples were incubated at 37 ° C in Proteinase K (dilution 1: 30, Millipore Corporation) for 40 min. and then waited in the laboratory until the room was warmed up. The LAB-SA Detection System, (Histostain-Plus Bulk Kit, Invitrogen) was applied to determine immunohistochemical localization of 8-hydroxydeoxyguanosine (8-OHdG) in tissues. Slides were incubated with polyclonal goat anti-8-Hydroxydeoxyguanosine (8-OHdG, Millipore Corporation) antibody, which was diluted 1:200 for the stomach tissue, for 30 minute at room temperature. Diaminobenzidine-

tetra hydrochloride (DAB, Invitrogen Corporation) was used as the colorant. Also Mayer's hematoxylin stain was used as a nuclear counterstain.

Dye samples were evaluated on the Zeiss AXIO Scope 1 brand research microscope. Analysis of 8-OHdG immunoreactive cells in the stomach tissue was performed using the Leica LAS V3.8 image analysis system. Five of the sections from the blocks containing the stomach tissues of all the rats in all groups were stained. From the stained sections, 1000 cells were counted and immunoreactive cells were identified among these cells. Tosun et al. (2006); Bakır et al. (1996); Avunduk et al. (2000) for this purpose;

Immunopositive cells / Total cell count (1000) -------- x 100 % = ….. % formula were used .

2.4. Statistical analysis

SPSS 15 version was applied for the statistical evaluation of the results obtained with the applied formula. Kruskal-Wallis Test was used for nonparametric tests to determine the differences between survivin immunoreactivity groups. The difference between the groups was considered significant in the results of $p < 0.05$.

3. RESULTS

There was no significant change in the staining of the stomach of the rats in the first group with Hematoxylin & Eosin (Figure 2).

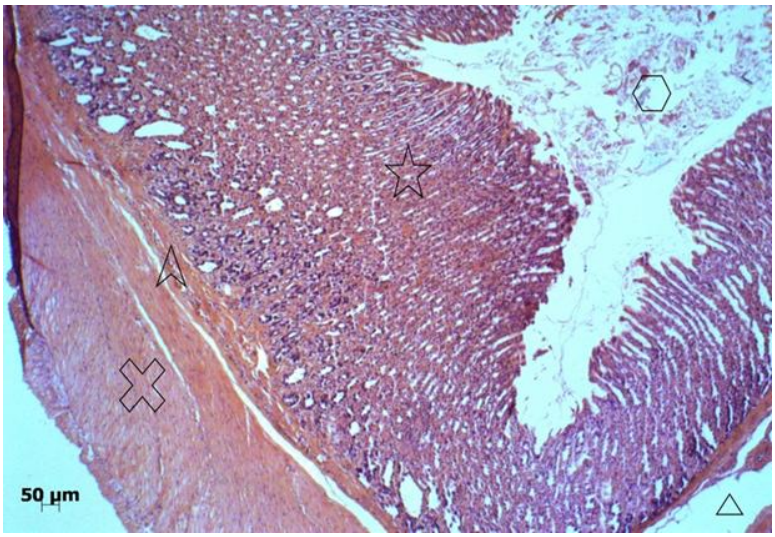

Figure 2. For the first study group was the control group; standard rat diet was given every days. Rat stomach, (H.E.x5). **Star**: Lamina propria mucosa; **Pointed arrow**: Lamina muscularis mucosa; **Arrow head**: Lamina submucosa; **Crossed:** Tunica muscularis; **Hexagon**: Gastric lumen

In the second group, there were active chronic gastritis findings in the rat gastric mucosa (Figure 3). Mononuclear inflammatory cells were observed lamina propria mucosa, lamina muscularis mucosa and lamina submucosa.

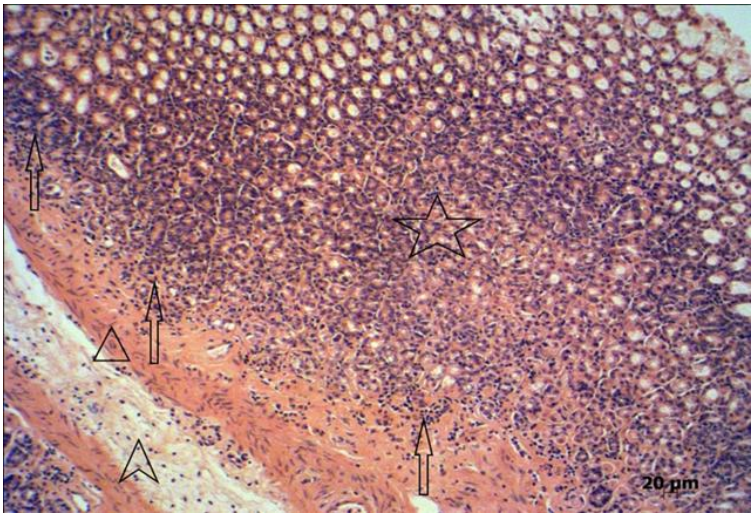

Figure 3. For the second study group; 75% carpet shell clam + 25% standard rat diet standard rat feeds were given daily. Rat stomach, (H.E.x10). **Star:** Lamina propria mucosa; **Arrow head:** Lamina muscularis mucosa; **Pointed arrow**: Lamina submucosa; **Arrows**: Mononuclear inflammatory cell.

In the third group, mononuclear inflammatory cells were observed in some areas of the lamina muscularis mucosa, more in the lamina propria mucosa (Figure 4).

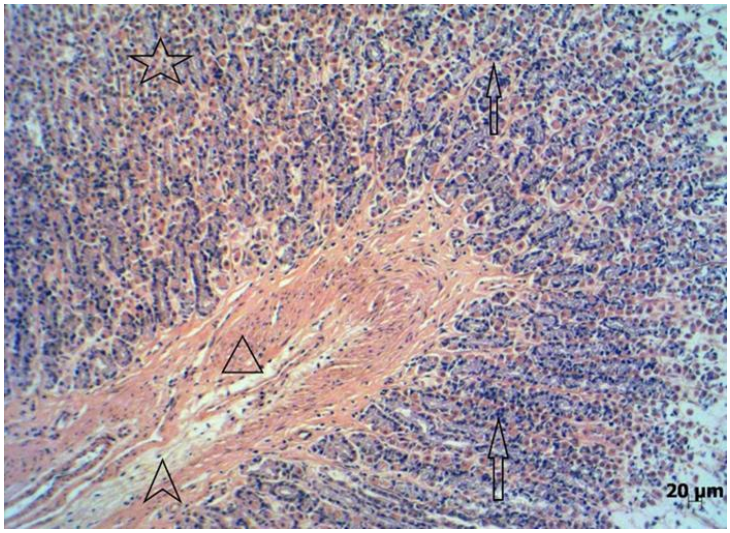

Figure 4. For the third study group; 75% carpet shell clam + 25% standard rat diet was given every two days. Standard rat diet was given the other day. Rat stomach, (H.E. x10). **Star**: Lamina propria mucosa; **Arrow head**: Lamina muscularis mucosa; **Pointed arrow**: Lamina submucosa; **Arrows:** Mononuclear inflammatory cells.

In the fourth group, while mononuclear inflammatory cells were observed mildly on the lamina propria mucosa, lamina muscularis and lamina propria were more common on the border. (Figure 5).

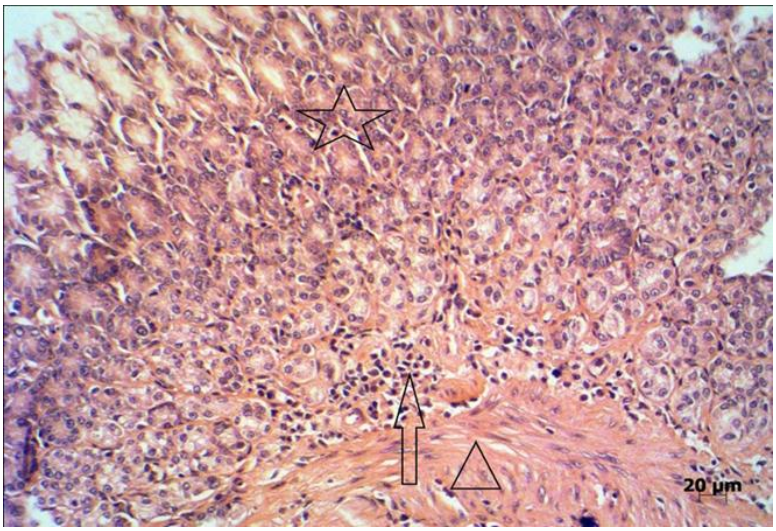

Figure 5. For the fourth group; 75% carpet shell clam + 25% standard rat diet was given every three days. Standard rat diet was given the other two day. Rat stomach, (H.E.x20). **Star:** Lamina propria mucosa; **Arrow head:** Lamina muscularis mucosa; **Arrow:** Mononuclear inflammatory cells

8-OHdG immunoreactivity was negative in stomach tissues in all groups. No significant differences were detected between groups in immunohistochemical staining with 8-OHdG (Figure 6).

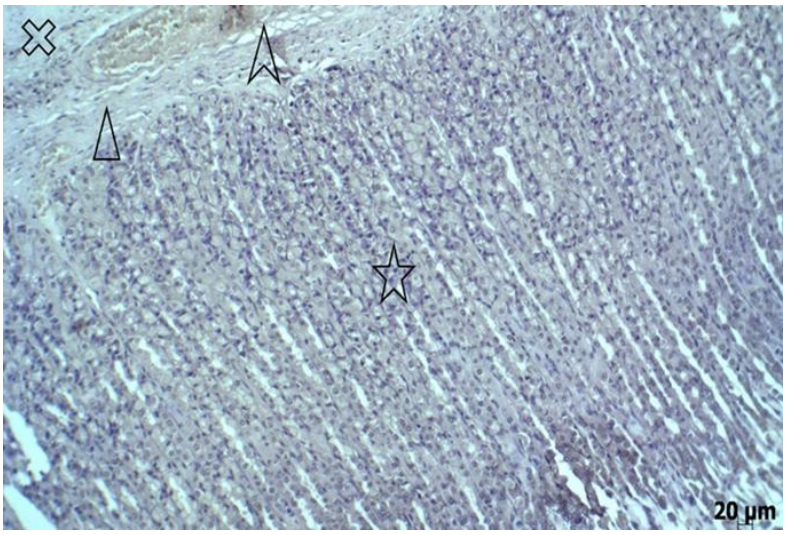

Figure 6. For the second study group; 75% carpet shell clam + 25% standard rat diet standard rat feeds were given daily. Rat stomach. (8-OHdGx10). **Star:** Lamina propria mucosa; **Arrow head:** Lamina muscularis mucosa; **Pointed arrow:** Lamina submucosa; **Crossed:** Tunica muscularis.

4. DISCUSSION

In this study, we found mononuclear inflammatory cell growth and chronic gastritis in the gastric tissues of rats which are fed with carpet shell clam that are collected from the Çardak Lagoon (Çanakkale, Turkey).

Heavy metals are commonly found in the environment and diet. In small amounts they are required for maintaining good health but in larger amounts they can become toxic or dangerous. Heavy metal toxicity can lower energy levels and damage the functioning of the

brain, lungs, kidney, liver, blood composition and other important organs. Long-term exposure can lead to gradually progressing physical, muscular, and neurological degenerative processes that imitate diseases such as multiple sclerosis, Parkinson's disease, Alzheimer's disease and muscular dystrophy. Repeated long-term exposure of some metals and their compounds may even cause cancer (Jarup, 2003). The toxicity level of a few heavy metals can be just above the background concentrations that are being present naturally in the environment. Hence thorough knowledge of heavy metals is rather important for allowing to provide proper defensive measures against their excessive contact (Ferner, 2001). Heavy metals are toxic because they may have cumulative deleterious effects that can cause chronic degenerative changes (Ibrahim et al. 2006), especially to the nervous system, liver, and kidneys, and, in some cases, they also have teratogenic and carcinogenic effects (IARC, 1987). Long-term exposure to heavy metals such as mercury (Hg), lead (Pb), chromium (Cr), cadmium (Cd), arsenic (As), copper (Cu), vanadium (V), nickel (Ni) chronic inflammation, cardiac, pulmonary and neurological effects and some cancers (Nieboer et al. 2013; Mantovani et al. 2008; Clarkson, 2002). Recent studies have shown that vascular effects of heavy metals may contribute to a variety of pathologic conditions including diabetes mellitus and hypertension (Navas-Acien et al. 2005; Prozialeck et al. 2006). In this study, we found mononuclear inflammatory cell growth and chronic gastritis in gastric mucosa of rats fed with carpet shell clam. Findings by some investigators that heavy metals may cause inflammation support our findings.

Reactive oxygen species cause more than 20 oxidative base damage products in DNA (Dizdaroğlu, 1998). Among these bases, 8-hydroxy-2'-deoxyguanosine (8-OHDG) is highly sensitive and the most common oxidative DNA damage (De Martinis et al. 2002). Some researchers have found that heavy metal salts can cause DNA damage (Fraga et al. 1990; Halliwell, 2000; Williams et al. 2000; Ateş et al. 2004; Burçak et al. 2004; Siomek et al. 2006). Immunohistochemical staining methods are used to detect cell and tissue damage (Gezen, 2017). In this study, we investigated whether or not to produce DNA damage by feeding the carpet shell clam containing heavy metal salts to rats. However, 8-OHDG was found to be negative in the gastric mucosa of all groups in our study. It is thought that heavy metals in low levels (NOEL) in the grains do not cause DNA damage.

However, the histopathologic changes in the gastric mucosa of the carpet shell clam fed rats assumes that gastrointestinal diseases are highly likely in people who consume these carpet shell clam. The authors think that care must be taken when consuming this kind of seafood.

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Footness

* At the time of this research, she was working at Department of Pathology of Çanakkale Onsekiz Mart University.

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ANALYSIS OF THE HIGH COURT DECISIONS ON INFORMED CONSENT CASES IN TURKEY FROM A FORENSIC POINT OF VIEW

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ABSTRACT

Informed consent is linked to the principle of patient autonomy and has an important place in common medical codes of conduct and legislative regulations. The aim of this study is to determine the judgments and reviews of the high court (Yargıtay) related to informed consent and to discuss them from a medicolegal aspect within Turkish jurisprudence. In the search engine of the website publishing high court decisions, the keywords "informed consent", "information", "consent" and "assent" were used without any date limitation. In this study, N=32 high court judgments were investigated. The data obtained were analyzed in light of the literature and guidelines. In 23 of the cases (71.9%) surgical interventions requiring general anesthesia were performed. In the other 9 cases (28.1%) surgical interventions not requiring general anesthesia and medical interventions with diagnostic and/or treatment purposes were performed. There was a statistically significant difference between the groups with informed consent and without informed consent for "surgical interventions not requiring general anesthesia and medical interventions with diagnostic and/or treatment purposes". The high court identified that in 17 of the cases (53.1%) informed consent was not present while in 15 (46.9%) informed consent was obtained. The court could not prove that informed consent was obtained in 15/17 cases in the group without consent, while in 7/15 cases in the consent group inadequate informed consent was obtained. The high court interrogated the extent and adequacy of informed consent for all types of surgical interventions both requiring and not requiring general anesthesia and medical interventions with diagnostic and/or treatment purposes. The types of surgical and medical interventions that require written informed consent and the aims of informed consent should be re-evaluated.

1. INTRODUCTION

Patients have the right to make decisions related to surgical and medical interventions to be performed on them and this right has an important place in common medical codes of conduct and legislative regulations (Williams, World Medical Association-WMA-Medical Ethics Manual, 2005). The Biomedicine (Oviedo) Convention approved by Turkey in 2003 gives the following general rule related to consent: *any intervention in the area of health shall be performed after consent is given by the relevant individual freely and after being informed about the intervention* (Council of Europe, Oviedo/Biomedicine Convention, 1997; Yılmaz, 2015). In fact, the topic of "consent" is not a new one in Turkey. Pertaining to the

Performance of the Art of Medicine and its Branches Law dated to 1928 states that: *Doctors shall obtain consent from the patient for all medical interventions. For large surgical interventions this consent must be written* (Art of Medicine Law, 1928). Currently the Professional Ethics Rules of the Turkish Medical Association (TMA) and the Ministry of Health Patient Rights Regulations include basic regulations related to obtaining informed consent from patients (TMA-Professional Ethics Rules of Medicine 1999; Patient Rights Regulation 1998/2014).

Informed consent may result in accepting or rejecting medical interventions or choice between treatment options (Williams, WMA Medical Ethics Manual, 2005). The information process basically involves informing the patient sufficiently about their disease and possible treatment options so they can make decisions related to treatment (Turla *et al.,* 2005). When examined from this aspect, the informed consent process is defined as sufficiently informing the patient, letting them consider the situation within the bounds of possibility and freely making a decision (TMA Informed Consent Guide, 2010). Consent obtained after inadequate information is accepted as legally void (Türker *et al.,* 2019). In the literature, there are many cases of doctors being sued for malpractice due to obtaining inadequate consent, or not obtaining written informed consent or not obtaining informed consent (Küçüker, 2012; Tümer and Dener, 2006). These cases related to informed consent are not only relevant to surgical branches. For example, according to a research, the rate of inadequate informed consent in dermatology is 20% (Ogawa *et al.,* 2008). In recent years in Turkey, there are many high court decisions related toinformedconsentknown (Oral, 2011; Gülel, 2011). In the literature there are researches investigating court decisions related to malpractice (Can *et al.,* 2011, Cakmak*et al.,* 2017); but there is no research discussing the medicolegal dimension of casesrelated to informed consent. This research will contribute to remedy this deficiency in the literature. The aim of this study is to discuss decisions and criticisms of the high court related to informed consent from a medicolegal aspect.

2. MATERIAL AND METHODS

2.1. Research design and population

This research is a descriptive, cross-sectional study and retrospectively screened decisions by the high court that represent a precedent about informed consent. The investigated decisions were accessed using the search engine on the high court website (Court of Cassation/Yargıtay, 2018). This website included the decision summaries of cases heard by the high court. While screening the decisions there was no date limitation. In this research, cases related to informed consent where the verdict of the local courts was overturned or upheld were investigated. The inclusion criteria for the cases were: i) whether informed consent was obtained or not obtained, ii) whether information and documents related to informed consent were present in the files or not, iii) whether the local court or expert reports investigated the topic of informed consent or not, iv) whether informed consent for performed medical interventions were adequate or not, and v) the Biomedicine (Oviedo) Convention, TMA Professional Ethics Rules for Medicine or other relevant legal regulations were cited.

2.2. Application of the Research

In this research, court decisions open to the public and published on the internet by the Court of Cassation were investigated with no ethics committee permission obtained. The decisions were accessed from the high court website (Court of Cassation/Yargıtay, 2018). In the search engine, the keywords “informed consent”, “information”, “consent” and “assent” were used without any date limitation. The screening accessed 34 decisions. There were 32 cases abiding by the inclusion criteria for the study which were investigated with the aid of a

data collection form. The descriptive characteristics of the research group, surgical and medical interventions, criticisms related to informed consent and data belonging to the legal basis for these criticisms of the Biomedicine (Oviedo) Convention and TMA Professional Ethics Rules for Medicine and other legal regulations were analyzed.

2.3. Data collection tools

Data belonging to the study group were obtained based on variables included in the data collection form and all data was transferred to a statistical analysis program. The variables analyzed in this study of sociodemographic data, event and court dates, court type, surgical and medical interventions, content of expert reports, criticisms and judgments of the high court related to informed consent, and variables belonging to relevant international and national legal regulations varied according to the features of the event.

2.4. Statistical analysis

Analysis of data obtained in this research used the Statistical Product and Service Solutions (SPSS) (version 20.0; SPSS /IBM Inc., Chicago, IL, USA) program. Descriptive data of number, percentage, mean, standard deviation, median, minimum and maximum values are presented. The correlations between variables were assessed with the Pearson Chi-square test and significance was assessed with the T test. Statistical significance was accepted as $p<0.05$.

2.5. Limitations of the Research

This research to reveal the deficiencies and errors related to informed consent attracts attention to the importance of applying standards in medical interventions but may increase the possibility of other medical errors being missed. With the aid of the investigated sample, an important perspective on the legal approach to informed consent in Turkey is revealed; however, the small size of the sample may prevent generalization of the results. It was determined that some descriptive characteristics were missing in the cases of the high court. For example, the ages and genders of all cases could not be determined. Using the available data and characteristics of the case, an attempt was made to determine the approach of the high court to scope and adequacy of informed consent.

3. RESULTS

In this research, N=32 high court judgments were investigated. According to the accessible data, 10 cases were female (76.9%), 3 were male (23.1%) and mean age was 30.0±10.0 (n:5, min:13-max:39) years. The mean duration of cases was 6.7±10.0 (n:32, min:2.6-max:11.8) years. When the legal basis cited in the cases are investigated, 19 (59.4%) cited the Biomedicine (Oviedo) Convention, 19 (59.4%) cited the TMA Professional Ethics Rules of Medicine, 1 (3.1%) cited the Patient Rights Regulation and 1 (3.1%) cited the Pertaining to the Performance of the Art of Medicine and its Branches Law (Table 1). Of the 32 cases investigated, 3 (9.4%) were determined to involve death, 8 (25%) life-threatening event, and 19 (59.4%) permanent functional disorder or loss. There was no statistically significant difference in terms of case duration between cases involving death, life-threatening event, and permanent functional disorder or loss ($p>0.05$). Of interventions performed, 23 (71.9%) were surgery requiring general anesthesia (Table 1) and these included 4 nose operations, 3 births, 3 laser eye surgeries, 2 spinal surgeries, 2 breast reductions and abdominoplasty, 1 liposuction and abdominoplasty, 1 breast enlargement, 1 laparoscopic appendectomy, 1 knee operation, 1 triple arthrodesis (ankle) surgery, 1 tonsillectomy, 1 thyroidectomy, 1 surgeryand 1 teratoma-linked retroperitoneal cyst excision. Of cases, 9 (28.1%) were surgical interventions not requiring general anesthesia and medical interventions with diagnostic and/or treatment purposes (Table 1); these included 2

colonoscopies, 1 angiography, 1 hemorrhoidal electrocoagulation, 1 filler material injection, 3 injections and 1 laboratory test (beta HCG). According to expert reports, for 26 cases (81.3%) the results were determined to be complications, with no assessment on this topic for the other 6 cases. Expert reports stated there was no medical intervention error in 23 cases (71.9%), with 2 cases (6.3%) obtaining signed informed consent and 1 case (3.1%) with no informed consent obtained. Of the investigated cases, 17 (53.1%) did not have informed consent obtained and 15 (46.9%) did have informed consent obtained. Between the groups with and without informed consent, there was a statistically significant difference identified in terms of "surgical interventions not requiring general anesthesia and medical interventions with diagnostic and/or treatment purposes" ($p<0.05$). When the decisions and criticisms of the high court about the 15 consent cases (46.9%) are investigated, 8 cases (25.0%) were assessed as adequate informed consent while 7 (21.9%) were determined to be inadequate informed consent (Table 1).

Table 1. Descriptive characteristics, medical expert reports and high court judgments of investigated cases

Investigated high court judgments (%)*	32 (100.0%)
Age (mean ±SD*)(of cases with age stated)	30.0±10.0
Gender(female), n (%)* (of cases with gender stated)	10 (76.9%)
Gender(male), n (%)*(of cases with gender stated)	3 (23.1%)
Case duration (mean±SD*)	6.7±10.0
Legal basis cited by court	
Biomedicine (Oviedo) Convention	19 (59.4%)
TMA Professional Ethics Rules for Medicine	19 (59.4%)
Patient Rights Regulation	1 (3.1%)
Pertaining to the Performance of the Art of Medicine and its Branches Law	1 (3.1%)
Types of intervention	
Surgical interventions requiring general anesthesia	23 (71.9%)
Surgical interventions not requiring general anesthesia and medical interventions with diagnostic and/or treatment purposes	9 (28.1%)
Results of medical expert reports	
Result occurring was complication	26 (81.3%)
No surgical or medical intervention error	23 (71.9%)
Signed informed consent given	2 (6.3%)
Lack of informed consent as deficiency	1 (3.1%)
Informed consent procedure according to high court	
Informed consent not present**	17 (53.1%)
Informed consent obtained	15 (46.9%)
Adequate informed consent	8 (25.0%)
Inadequate informed consent	7 (21.9%)

*: SD: standard deviation; n: number; %: percentage.**:consent not obtained, no information/documentary proof and fake consent

The decisions of the court related to the 17 cases (54.8%) without informed consent were that in 1 case informed consent was not obtained and in 10 cases there were no information or documents showing informed consent was obtained. For 5 cases it could not be proven that informed consent was obtained and in 1case fake informed consent documents were created. The criticisms and decisions of the high court related to informed consent are shown in Table 2.

Table 2. Decisions and criticisms related to informed consent of the high court according to types of intervention			
Decision and Criticism of the high court		**Types of intervention**	
IC*not obtained		Hemorrhoidal electrocoagulation	
No IC document in file, no discussion of whether IC was obtained or not in expert reports		Breast enlargement	
IC document present. In the form of printed consent form. IC document **insufficient** as evidence		Laser eye surgery	
Not proven that IC was organized		Laser eye surgery	**Injection**
		Nose surgery	Knee surgery
No information or document about information in the file.		**Colonoscopy**	**Beta HCG test**
		Spinal surgery	
IC document present. Treatment, success rates and duration, risks, medical results and possible complications explained		Laser eye surgery	
Written IC document present. Medical results and possible complications explained. However, no explanation (inadequate) of treatment, success rates and duration, risks, medical results and possible complications		Nose surgery	Thyroidectomy
		Breast reduction and abdominoplasty	
Not sufficiently informed**	**IC document present.** Side effects and complications reported with general statements; however no explanation of what types of complications occur with this type of surgery	Nose surgery	
	Written IC document present. Medical results and possible complications explained. However, no explanation of treatment, success rates and duration, risks, medical results and possible complications	Breast reduction and abdominoplasty	
	Written IC document present. Medical results and possible complications explained. However, not sufficiently informed about health problems experienced	Tonsillectomy	
Whether IC was obtained should be investigated	No IC document in file	**Injection**	Spinal surgery
		Birth	Triple arthrodesis
Information about complications could not be proven with written document		Filler material injection	
No IC document in file. Firstly IC form signed by patient should be obtained		**Injection**	**Angiography**
Fake IC form created		Surgery	
Consent on patient's admission paper. Necessary information about the quality and probable risks of surgery not given (**inadequate**).		Nose surgery	
IC document present. Diagnosis, surgery and possible risks should be explained and IC obtained.		Retroperitoneal cyst excision	
IC document present. Diagnosis, procedure and possible risks clearly explained.		**Colonoscopy**	Birth
IC document present. IC obtained for selection of surgical technique		Laparoscopic appendectomy	
IC document present. Informed consent form including possible complications arranged.		Birth	
IC document present. However, proof of information about risks of surgery **inadequate**.		Liposuction and abdominoplasty	
*IC: informed consent, **: Scope of informed consent inadequate.			

4. DISCUSSION

In this research, the judgments of the high court in Turkey related to informed consent were investigated from the medicolegal aspect. In this study, 23 cases (71.9%) were surgical interventions requiring general anesthesia and 9 (28.1%) were surgical interventions not requiring general anesthesia and medical interventions with diagnostic and/or treatment purposes. There was a statistically significant difference identified between the groups with and without informed consent in terms of "surgical interventions not requiring general anesthesia and medical interventions with diagnostic and/or treatment purposes". According to high court judgments, 17 cases (53.1%) did not involve informed consent and 15 (46.9%) did involve informed consent. Of the group without consent, the court stated that in 15/17 cases there was no information or document proving informed consent was obtained. Of the group with consent, the court found adequate informed consent was obtained in 8/15 cases and inadequate informed consent was obtained in 7/15 cases. According to the results of this research, the high court in Turkey interrogated "whether informed consent was obtained or not" and "the extent and adequacy of the consent" for all cases including those with surgical interventions not requiring general anesthesia and medical interventions with diagnostic and/or treatment purposes.

The literature related to informed consent reports that inadequacy of informed consent is common in Turkey (Gündoğmuş et al., 2005). In 93 surgical malpractice cases informed consent was not obtained from the majority of patients (Tümer and Dener, 2006).A group surgical malpractice case found 31.9% developed thyroid pathology and 44.7% had laryngeal nerve injury and informed consent was not obtained from the majority of these cases (Eş et al., 2017).Informed consent was not obtained in 19% (4 cases) of eye surgery cases (Özdemir et al., 2014). In this research, the high court found informed consent was not obtained for 17 cases (53.1%) and identified that 15 of these 17 cases did not have any information and documents proving informed consent existed in the case file. For some cases, the court stated it was necessary to firstly research whether the patient was informed or not and then obtain the informed consent document. In medical malpractice cases insufficient and unreliable records are an important argument used by plaintiffs (Altun and Yorulmaz, 2010). For cases related to plastic surgery interventions (Vila-Nova da Silva et al., 2015; Hwang et al. 2018), the main factors severely affecting court judgments were stated to be the quality of medical records and informed consent, and photographs from before and after surgery. In this research analyzing high court judgments in Turkey, the majority of interventions were surgical; however, among these there were several plastic surgery interventions and 9 (28.1%) were surgical interventions not requiring general anesthesia and medical interventions with diagnostic and/or treatment purposes. In the whole group analyzed, though expert reports stated that the majority of negative results harming the patients' health were complications, the high court questioned whether informed consent was obtained or not for all medical applications including injections. In 15 cases (46.9%) informed consent was identified and nearly half of these were determined to be inadequate informed consent. These results reveal the importance of the quality of medical records and informed consent in terms of the courts.

According to legal regulations in Turkey, written informed consent is required for large surgical interventions, organ transplants, curettages and sterilizations, situations where reproductive-assisting treatments are applied and researches using human subjects (Gülel, 2011;Tümer et al., 2011; Demir, 2017). However, written consent is not requested for applications like injections, vaccinations and wound dressing (Tümer et al., 2011). There are different approaches among countries in relation to the written informed consent procedure. For example, while there is no written informed consent obligation for any medical practice in Denmark, this is a legal requirement in Portugal (Tümer et al., 2011).Minor procedures may

only require verbal consent in Australia (Australian Commission on Safety and Quality in Health Care, 2012). In the present study, the high court identified that for some surgical interventions requiring general anesthesia, there was no information or documents about whether informed consent was obtained in the case files. Additionally, patient informed consent was not obtained for "surgical interventions not requiring general anesthesia and medical interventions with diagnostic and/or treatment purposes" and this was statistically significant. Cases not requiring general anesthesia included 2 colonoscopies, 1 angiography, 1 hemorrhoidal electrocoagulation, 1 filler material injection, 3 injections and 1 laboratory test (beta HCG). According to the high court in Turkey the doctor or the hospital should prove that the patient was informed. One of the noteworthy results identified in this research is that for injections and any biochemical testing, informed consent was interrogated. The Patient Rights Regulation, updated in recent years, mentions that written consent should be obtained for medical interventions predicted to cause disputes, apart from the situations stated in law (Patient Rights Regulation, 1998/2014). The consent form should state that information has been verbally explained to the patient and two consent forms are signed with one given to the patient (Patient Rights Regulation, 1998/2014; Türker et al.,2019). In some clinics in Turkey, doctors avoid legal disputes by obtaining written informed consent for even the simplest procedures and this type of approach is stated to negatively affect the functioning and coverage of medical practice (Tümer et al., 2011). According to these results, it is considered necessary to re-evaluate which types of intervention require written informed consent and the aim of informed consent.

In the literature, some studies have discussed the topic and limits of giving sufficient information in relation to the adequacy and quality of informed consent (Turla et al., 2005; Turla et al. 2006; Oral, 2011). Different results from research of patients are noteworthy; one research found 22.7% of patients were not given information about surgery, 18.3% were not informed of disease diagnosis, 52.3% were not informed of the name of the surgery, 12.5% were not informed about possible complications during surgery and 13.7% were not informed about postoperative complications (Kurt et al., 2016). Another study reported that all patients signed informed consent forms, 80% received important information about disease, 62% received information about the surgery, 56% were informed in writing (in person or with the aid of a relative), 28% received information about possible complications of surgery and 85% did not receive information about alternative treatments (Ekmekçi et al., 2016). Another research reported 85% of patients did not know how long they would stay in hospital after surgery, while 83% were not given information about possible changes to their lives after surgery (Turla et al., 2005). A research investigating informed consent forms found 81.3% had the risks of treatment in writing, while 33.1% had alternative treatment methods in writing (Küçüker, 2012). The judgments and reviews of the high court (Yargıtay) about inadequate informed consent were as follows in the present study: "necessary information about the quality of the surgery and possible risks were not given; patients not sufficiently informed about health problems experienced; side effects and complications reported in general statements but the type of complications of this type of surgery not explained in detail; and no explanation of treatment, chance of success and duration, risks, medical results and possible complications".

5. CONCLUSIONS

These results reveal the importance of the informed consent process. It appears necessary to assess recommendations related to the consent process, like the right of the patient not to be informed, noting patient benefit from all medical interventions, effect of diagnosis and information on the patient's health, use of short and understandable language for informing the patient, developing multi-media resources, use of visual material like videos

and photographs, and inclusion of patients in the informed consent form development process (Art of Medicine Law 1928; TMA Professional Ethics Rules in Medicine 1999; Patient Rights Regulation 1998/2014; TMA Informed Consent Guide, 2010;Council of Europe, Oviedo/Biomedicine Convention, 1997; Williams, WMA Medical Ethics Manual, 2005; Turla et al., 2005; Tümer et al., 2011; Kurt et al., 2016; Ekmekçi et al., 2016).

In conclusion, it is considered necessary to rethink the aim of informed consent of the patient and to consider this question: is the basic aim of informed consent to protect doctors from malpractice cases or to ensure participation in the decision-making process by observing principles of patient benefit and autonomy?

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Abbreviations

Art of medicine law: Pertaining to the Performance of the Art of Medicine and its Branches Law (Tababet ve Şuabatı San'atlarının TarzıİcrasınaDair Kanun, No.1219).

Biomedicine (Oviedo) Convention: Convention for the protection of human rights and dignity of the human being with regard to the application of biology and medicine: convention on human rights and biomedicine (CETS No. 164), Oviedo.

TMA: Turkish Medical Association.

WMA: World Medical Association.

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THE CONCEPT OF CARRYING CAPACITY IN TERMS OF SUSTAINABLE USE POLICIES: A CASE STUDY OF BAYRAMİÇ AYAZMAPINARI NATURAL PARK (ÇANAKKALE, TURKEY)

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ABSTRACT

The idea underlying the understanding of sustainability is that mankind should live in such a way that will not exceed the carrying capacity of the environment in order to support it. That is, the sustainable management of natural resources is the way to attain sustainable development. On the other hand, ecological sustainability can be achieved only through conservation-based scientific approaches. If the problems to be caused by the uncontrolled use of resources are predicted in advance and if planning is made to this end, the sustainable use of protected areas will be possible. The concept of "carrying capacity" and the planning studies carried out within the framework of this concept are also essential to hand protected areas down to the future.Within the framework of this study, it was intended to determine the carrying capacity of Bayramiç Ayazmapınarı Natural Park, which was taken under conservation with the "Natural Park" status in 2011 and which plays an important role in the economic development of the locality. "The Method of Estimating the Carrying Capacity in Protected Areas", recommended by the IUCN, was employed in the research, which was carried out to ensure the sustainable use of the study area with important natural and cultural landscape assets. As a result of the method, it was established that Bayramiç Ayazmapınarı Natural Park had some intensity of use above its carrying capacity. It was concluded that the intensive tourism activities creating a rather negative situation in terms of the sustainability of resources should be re-planned on the basis of conservation & use. Proposals of conservation policies were made in order to hand the existing natural and cultural landscape assets down to future generations. Furthermore, the incomplete or wrong uses in the area were highlighted and various suggestions were made to this end in the research.

1. INTRODUCTION

Although the idea of conservation of featured areas dates back to centuries earlier, the evaluation of conservation decisions on a legal basis commenced more recently. It might be stated that the first systematic approach to this matter started with the declaration of Yosemite National Park in the U.S.A. in 1872. Following this, many countries declared protected areas

on various scales. In this process, many environmental organizations were founded and various studies were presented due to the extensive framework of the concept of "conservation". The International Union for Conservation of Nature (IUCN), the largest of these organizations, was founded in 1948. With its 16,000 voluntary-specialized employees in total, it prepares guides in the international sense with regard to the definition and categorization of protected areas (URL 1). Within the framework of these guides, the IUCN defines a protected area as "a clearly defined geographical space, recognized, dedicated and managed, through legal or other effective means, to achieve the long-term conservation of nature with associated ecosystem services and cultural values" (URL 2).

In addition to this system by the IUCN, the categories of "Biosphere Reserve Sites" and "World Heritage Sites", defined by the United Nations Educational, Scientific and Cultural Organization (UNESCO), are available, and in addition to all these conservation classes, there are also many studies on different scales such as the Ramsar Convention, Natura 2000, PAN Parks, and the Determination of Biogenetic Reserves.

The process of categorization of protected areas in Turkey commenced with Law No. 2873 on National Parks, dated 09/08/1983. The aim of the law is to organize the fundamentals of selecting and determining the national parks, natural parks, natural monuments, and nature conservation areas with assets at national and international levels in our country as well as of protecting, developing, and managing them without any degradation of their features and characters. In this law Natural Park is defined as "the pieces of nature which have the characteristics of vegetation and wildlife and which are favorable for the people to rest and be entertained in the scenic integrity" (URL 3).

The common goal of all these conservation studies, performed at both national and international levels, is to provide that the resource assets of local, regional or global importance in these areas can be handed down to future generations.

The developed transportation and communication possibilities, the changing understanding of tourism (e.g. nature-based tourism activities) and the business investments rapidly increasing to this end have turned many protected areas into important tourism destinations. The uncontrolled increase in tourism activities in some areas in this process was effective in taking conservation decisions.

Uithol (2000) states that when tourism is planned and monitored carefully, it may become a significant instrument for the sustainable development of protected areas and their surroundings (Güneş, 2008). Especially given the scarcity of the income earned from the existing agricultural activities and the labor exerted, the overwhelming majority of the local people welcome the arrival of more tourists. The demand for these areas has also brought about investment activities on various scales. Hence, the anthropogenic effect has been more intensive in protected areas and their close vicinity. Nevertheless, the use of resources in such a way that is distant from conservation-based approaches and that allows obtaining maximum income in the short term leads to irreversible damage. In addition, although tourism initially satisfies the local people in terms of economic income, the incoming visitors cause various problems in the original and traditional life at the locality, which causes the people to have a negative attitude towards tourism.

At this point, the concept of sustainability has gained great importance for protected areas. According to Tekeli (2001), sustainability is a moral principle which originated within the environmental movement, which is quite widely accepted, and whose content is continually being intended to be re-determined in the political process (İncedayı, 2004). According to Kalem (2001) and Sethi (1999), the idea underlying the understanding of

sustainability is that mankind should live in such a way that will not exceed the carrying capacity of the environment in order to support it. That is, the sustainable management of natural resources is the way to attain sustainable development. According to this understanding,

*the maintaining of ecological processes and the providing of continuity,

*preservation of biodiversity,

*the ensuring of equality among and within present and future generations and

*integration of social, environmental, and economic approaches constitute the fundamental principles of sustainable development (Güneş, 2008).

As Edwards (2005) indicated, the paradigm of sustainability was extensively presented in the report by the World Commission on Environment and Development in 1987 (Laven et al., 2015). In the same report (Our Common Future – the Brundtland Report), meeting the present social, environmental, and economic needs without sacrificing the ability of future generations to meet their similar needs (Moldan et al., 2012). According to Richardson (1995), sustainable development is a concept which addresses ecological equilibrium and economic growth together and which both provides the efficient use of natural resources and attaches importance to environmental quality. The attainment of sustainable development in a country will take place through the attainment of ecological sustainability, economic sustainability, and social sustainability (Gürlük, 2001). On the other hand, ecological sustainability can be provided only through conservation-based scientific approaches. If the problems to be caused by the uncontrolled use of resources are predicted in advance and if planning is made to this end, the sustainable use of protected areas will be possible. The concept of "carrying capacity" and the planning studies carried out within the framework of this concept are also essential to hand protected areas down to the future.

2. THE CONCEPT OF CARRYİNG CAPACİTY

The first areas of application for the concept of carrying capacity are engineering and architecture. According to Çavuş, (2002), in the studies in these fields, the concept of carrying capacity was utilized as an instrument for planning so as to determine the capacity of physical structures (Soylu 2013). According to Sumner (1936), the first suggestion to apply the concept of carrying capacity to parks and similar areas was made in the 1930s. A National Park Report which made proposals of policies on parks in the California Mountains sought an answer to a question of what size of use there should be without any destruction of the basic features in natural areas (Manning, 2007). Moreover, in the report, it was recommended to confine the recreational use of natural areas to their carrying capacity. In a study on the recreational use of forests by Wagar in the following years, it was emphasized that the carrying capacity was crucial in all recreational activities in forests, particularly in intensively used areas. The first scientific application of the concept of carrying capacity in parks and similar areas was the studies carried out in the early 1960s by Wagar (1960) and Lucas (1964) (Manning, 2007). According to Fennel (2002), Lucas examined visitors' perceptions of wildlife in an area where the canoe sport was performed in his study in 1964 and suggested that the carrying capacity concerned environmental elements (Tokmak, 2008).

Since its first use, the concept of carrying capacity has been addressed under different conditions and in various disciplines by different circles, and many definitions have appeared. Even though the definitions have generally been similar, they have acquired different meanings according to the relevant discipline and their spheres of interest have expanded (Gül and Akten, 2005).

According to the World Tourism Organization (WTO) (1981), the Carrying Capacity is defined as the maximum number of people that may visit a tourism area at the same time, without any destruction of the physical, economic, and sociocultural environments and without any undesirable decrease in visitors' satisfaction levels (UNEP-PAP, 2009). In addition, again the WTO also stated that the carrying capacity was fundamental to environmental conservation and sustainable development (Avcı, 2007). Carey (1993) stated that the carrying capacity was initially developed regarding wildlife management and that it was based on the fact that an organism could only live under certain conditions. The number of organisms in an environment is determined by the accessibility to favorable conditions for life (McCool and Lime 2001). According to Wearing and Neil (1999), the concept of carrying capacity is generally used to express the threshold at which a system can absorb the changes (Liu, 2003). While the carrying capacity significantly affects the sustainability of the potential of an area for tourism, there are also some factors which affect the carrying capacity (Table 1) (Holden, 2000).

Table 1. The factors affecting the carrying capacity in those areas where tourism activities are experienced (Holden, 2000).

Factors affecting the carrying capacity
✓ Resistance of the landscape to development and change
✓ Existing development of, and infrastructural & superstructural possibilities for, tourism
✓ Number of visitors
✓ Type of tourists and their behavioral traits
✓ Environmental education levels of the local people and tourists
✓ The level of dependence of an area on tourism in economic terms
✓ Levels of unemployment and poverty
✓ Attitudes of the local people towards the environment and their opinions about the damage to the environment for a short-term gain
✓ The perspectives of local cultures and societies on extrinsic impacts and different lifestyles
✓ The organization level of destination management

It is possible to multiply the definitions of the carrying capacity. Although these definitions are quite similar to each other within a general framework, each type of carrying capacity has a distinct threshold value and different contents in terms of the development of tourism, as Liu (2003) also states. While Shelby and Heberlein (1984) related the carrying capacity to recreation and classified it as ecological, physical, social, and superstructural capacities, Pigram and Jenkins (1999) categorized the carrying capacity as physical, social, ecological, and economic capacities. On the other hand, O'Reilly (1986) grouped the carrying

capacity as economic, psychological, environmental, and social carrying capacities (Holden, 2000).

When different classifications in various studies are considered, it is seen that many researchers agreed on the categories of ecological (environmental in some sources), economic, social, psychological, and physical carrying capacities.

It might be stated that the ecological carrying capacity has the greatest share in terms of the sustainability of protected natural areas. Many different researchers made various definitions on the subject. The common ground in the definitions of the ecological carrying capacity is the occurrence of no irreversible degradation in any element of the ecosystem. The ecological carrying capacity is of great importance to manage tourism activities and recreational use and to provide sustainability in natural areas.

It is suggested that the ecological carrying capacity refers to the limit to the anthropogenic activities which will cause undesirable changes in the environment (Avcı, 2007). Considering this, Walson stated that the ecological carrying capacity was concerned with at what level of use the whole ecosystem from plants and animals to soil, water, air, and beach erosion would be affected at the level of certain uses as well as with what the cost of this use would be (Çavuş, 2004 as cited in Avcı, 2007).

By making a reference to Pigram (1983), Papageorgiou and Brotherton (1999) mentioned the ecological carrying capacity as the maximum level of recreational use sustained in terms of activities and numbers before the occurrence of any unacceptable or non-renewable falls in ecological values in a region or an ecosystem, whereas Buckley (1999) evaluated the ecological carrying capacity on the basis of the number of tourists which would not lead to any irreversible ecological changes.

Tourism activities substantially influence the economic level of the local people. When considered from this perspective, the economic carrying capacity is also a significant factor in providing sustainability. According to Çavuş (2002), when the concept of carrying capacity is evaluated in the economic sense, it might be stated that it is concerned with the economic activities in touristic regions and based on the approach to the sustaining of touristic activities without any negative changes in the quality and quantity of these activities (Tokmak, 2008). The economic carrying capacity is concerned with the level of use of an area or a facility with a certain financial yield (Papageorgiou and Brotherton, 1999) as well as with the balance between the benefits of tourism to the region and its cost (Avcı, 2007). Lim (1998) lists the factors affecting the economic carrying capacity as follows: investment, volume of tourists, cost of the holiday, level of economic benefits provided, level of enjoyment suited to the residents and others.

The social carrying capacity is a concept which is evaluated on the basis of users/visitors in those areas where there is intensive recreational use. The individuals performing recreational activities in any area may come from different sections of the society. Hence, they have a wide variety of demands and opinions about the features of an area. Moreover, the traditional lifestyles and habits of the local people may be positively/negatively affected by tourism movements and intensive use by visitors. Shelby and Heberlein (1984) evaluated the social carrying capacity particularly in terms of visitors and put forward some parameters to determine the social carrying capacity:

*Encounters with other parties per hour, day etc.;
*Number of encounters with groups of a particular size and type;
*Percent of nights camped away from others;
*Percent of attraction sites where people are out of sound and sight of others; and

*Number of people encountered at each attraction site.

Some of the above-mentioned parameters may vary by person. The social carrying capacity depends largely on personal perceptions. As Tokmak (2008) also states, starting from what point there will be a decline in the quality of experiences by tourists may display uncertainty. Even if it is accepted that under normal conditions, all other conditions (e.g. the environmental quality of the region, level of hospitality, overnight stay, catering, and entertainment possibilities) remain unchanged in a touristic region, a tourist may decide not to come to the region by thinking that the experience he/she has had in that region is enough and just so as to make a change.

Saveriades (2000) defines the social carrying capacity as the acceptable maximum level of use in an area without creating any dissatisfaction among visitors or any negative impact on the local people. Furthermore, he suggests that visitors' levels of satisfaction before they begin to seek a different destination and the levels of tolerance of the local people for the presence of tourists are two important components of the social carrying capacity.

In addition, it is rather difficult to know which of the impacts of tourism the local people will find unacceptable in the social sense and at what level. If studies to reveal these impacts in advance are carried out, it might be possible to go on using the land without exceeding the social carrying capacity values. Saveriades (2000) also states that the interaction among visitors, an area, and the local people living in an area gives rise to some social impacts and that these impacts are essential in the process of determining the deficiencies in capacity and adds that this point should be noted at the stage of planning.

Included in the concept of carrying capacity, the psychological carrying capacity is concerned with visitors' perception and levels of satisfaction. Thus, it is also used as the perceptual carrying capacity in some sources. Additionally, since perceptions by individuals play a significant role in this concept, the concepts of social carrying capacity and psychological (perceptual) carrying capacity may from time to time be used interchangeably as well. For instance, in their study, Lopez-Bonilla and Lopez-Bonilla (2008) considered them under the same heading as "social (psychological) carrying capacity". According to Tokmak (2008), the perceptual carrying capacity is closely related to tourists' satisfaction, while tourists' satisfaction is closely related to their expectations and purposes of coming to the touristic destination. Liu (2003) also addressed the psychological carrying capacity on the basis of visitors and related it to the perception and satisfaction by different tourists in different types of destinations and holidays.

The physical carrying capacity scrutinizes the issue particularly depending on the number of visitors and spatial adequacy. While Liu (2003) states that this concept is the maximum number of people that an area can hold, he expresses that the minimum quantity of area that a person may need is taken as the basis when making a numerical evaluation.

The physical carrying capacity not only means the maximum number of people who will use an area but also can be evaluated as the maximum equipment (e.g. a boat in a waterside recreational area) likely to be used in an area. This concept both may be a design concept and serves to create limits concerning security (the maximum number of users in any playfield). Moreover, the physical carrying capacity also provides indirect control on the number of users in any area (Pigram and Jenkins, 2006). Washburne (1982) states that many different elements (e.g. accessibility of the camping place at a campsite, situation and vegetation of the land, and the numbers of convenient campsites and of tents which can be used) might affect the physical carrying capacity in natural areas. Lim (1998) lists the factors affecting the physical carrying capacity of an area as follows: Area size, accessible space,

visual impact, climate, aesthetics, accommodation quality, availability of facilities, transportation, number of people that can be accommodated and others.

The tourism mobility in Bayramiç Ayazmapınarı Natural Park (BANP), an important protected area in the region with its natural resource assets, should be taken under control with a conservation-based approach. In this study, the area was scrutinized in many aspects including the situation of the physical conditions of the area in terms of recreational activities. The natural park was assessed within the framework of the concept of carrying capacity, and various predictions were made with respect to the future of the area. Furthermore, various suggestions were made for the existing problems of use, and design solutions were presented.

3. MATERIALS AND METHOD

BANP constitutes the main material of the study. In addition, various publications on the subject of the research, the previous studies on the study area, the maps, information, and documents procured from the institutions, the on-site observations and examinations and the photographs taken make up the rest of the study material.

BANP is at a distance of 91 km from Çanakkale and 23 km from the district of Bayramiç and remains within the borders of the Evciler Village (Figure 1). The area is located in the massif of Mt Kaz and at an altitude of 490 meters. Located between 39°44'51.1" - 39°44'41.5" northern latitudes and 26°50'49.1" - 26°50'32.6" eastern longitudes, the area covers a forest habitat with a size of 5.85 ha. The area was taken under conservation with the Natural Park status in 2011.

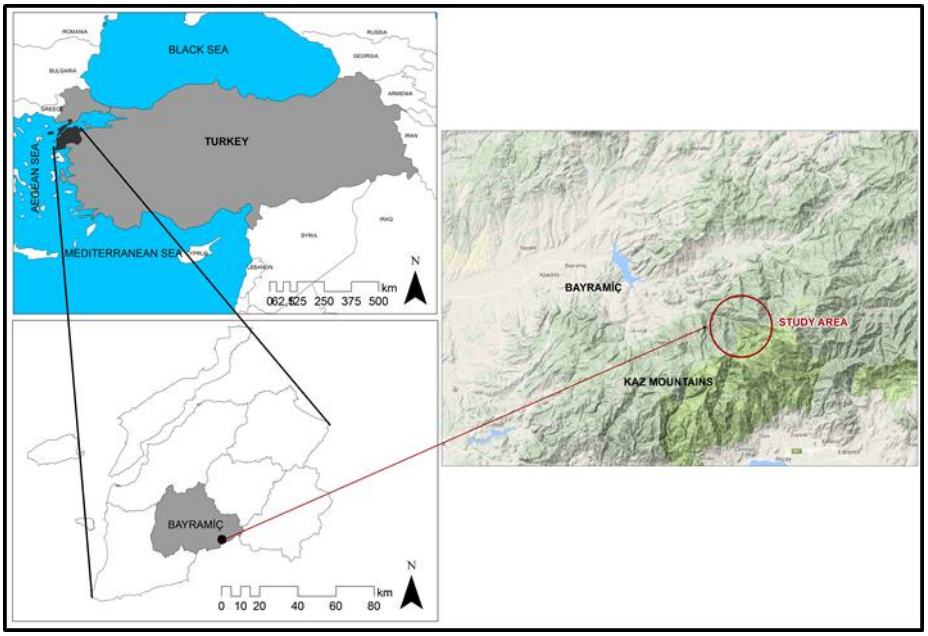

Figure 1. The geographical location of the study area (Database:1: ESRI maps, 2: Regional Directorate of Forestry, 3. www.atlas.gov.tr)

Pinus nigra stands constitute the dominant vegetation. Some vegetation which resembles that in the Black Sea Region is present along the Çınarcık and Ayazma Brooks – two important water bodies located in the area. Species *Castanea* sp., *Carpinus* sp., *Quercus* sp., *Platanus* sp., *Tilia* sp., *Fagus* sp. and *Corylus* sp. are encountered in these sections. The area is within the Marmara sub-climate type of the Mediterranean climate type. Accordingly, it has lower summer temperatures, quite cold winters, normal snowfall, more frequent freeze,

and a higher rate of cloudiness in comparison with the actual Mediterranean climate. This is a significant factor in recreationally preferring the study area in hot summer months. The study area has visually rich scenic examples together with its rich vegetation besides the brook passing through it and the resulting waterfall (Figure 2). Additionally, ecological tourism activities particularly like trekking in the forest are also among the activities frequently encountered in the area thanks to the richness of the biodiversity.

Figure 2. Waterfall and various images from the study area (Original, 2017).

The study area also has significant potential in cultural terms. As Koç (2008) also indicates, Mt Kaz and the Evciler Basin, where BANP is also located, constitute the mythological center for the Trojan Region and the source of all its riches and have a settlement past of over 6,000 years. The mythological sources mention that the first beauty contest on earth was held in Ayazma.

"The Method of Estimating the Carrying Capacity in Protected Areas", suggested by the IUCN and included in the study by Ceballos-Lascuráin (URL 4), was employed in the research. According to the method, three recreational carrying capacity levels are determined by using various parameters limiting visits in a formulation, namely "Physical Carrying Capacity", "Real Carrying Capacity", and "Effective Carrying Capacity". The formulae and explanations for these three carrying capacities are provided in Table 2.

The Physical Carrying Capacity (PCC) is the maximum number of people that can physically fit into a defined space at a specific time. The PCC is the multiplication of an area of 1 m^2 or a 1-meter-long trail per visitor by the total area which is open to visitors' use and the number of visits which may physically be paid within the working hours of the park per day.

The Real Carrying Capacity (RCC) is the maximum number of visits allowed in an area, and it is obtained by mathematically subtracting the correction factors obtained from specific negative features of the area from the PCC. These correction factors are obtained from biophysical, environmental, ecological, social, and managerial variables. According to the formula, the correction factors must be calculated first in order to find the RCC. The correction factors occur as a result of calculating the relationship between the limiting value of the factors which prevent or limit visiting and its total value with the method of interpolation. After all correction factors which are valid for the area have been calculated, they are mathematically subtracted from the previously calculated PCC. The correction factors expressed as percent values are put in their respective places in the formula.

The Effective Carrying Capacity (ECC) is the maximum number of visitors that an area can bear according to its existing management capacity. According to the formula, the ECC is the multiplication of the previously calculated RCC by the management capacity (MC). The MC is the sum of the conditions required in order for the management of a protected area to conduct its duties and objectives. It is not very easy to quantify the MC owing to the presence of a large number of variables such as legislation, infrastructure, superstructure and equipment, staff in number and quality, funds, and motivation. The ECC never turns out to be greater than the RCC.

Table 2. Formulation of the Carrying Capacity (URL 4)

Definitions	**Explanations**	
PCC = AxV/a x Rf	PCC	Physical Carrying Capacity
	A	Area (The existing area or trail for visitors' use)
	V/a	Visitor / area (Area or trail length per visitor)
	Rf	*(in the area: 1 visitor/m²; on the trail: 1 visitor/m)*
	Rf	Rotation factor (Number of visits per day) "The Rotation Factor" is the daily visits which are allowable in terms of the working hours in an area
		The period during which the area is open daily / The average duration of a visit
RCC = PCC - Cf_1 - Cf_2 -.....- Cf_n	Cf_1, Cf_2, Cf_n	Correction factors calculated for each variable
Cf = Vl / Vt X 100	Cf	Correction Factor (%)
= PCC x (100 – Cf1/100) x (100 - Cf2/100) x ..... x (100 - Cfn/100)	Vl	Limiting Value of the Variable
	Vt	Total Value of the Variable
ECC = RCC x MC	ECC	Effective Carrying Capacity
	RCC	Real Carrying Capacity
	MC	Management Capacity

4. RESULTS

The physical, real and effective carrying capacities of BANP were calculated within the framework of the method described in the Method section.

The Physical Carrying Capacity (PCC)

In order for visitors to tour the area in BANP, they must follow the route which consists of bridges and trails. The PCC-related features of the area:

- ✓ The linear length covered by a person on the trails: 1 m
- ✓ Total length of the trails: 550 m
- ✓ Duration of visit (on average): 5 hours
- ✓ Period during which the area is open to visits: 10 hours
- ✓ Maximum size of a group of visitors: 45 people
- ✓ Minimum spacing among the groups: 45 m

As the recommended minimum spacing among the groups is 45 m, 6 groups will fit into the 550-meter-long trails. Accordingly:

[(6groups x 45m) + (5 spaces x 45 m) = 495 m]. If these 6 groups visit the area at the same time, a total trail length of 270 m will be required. The rotation factor must be calculated to determine the PCC.

Rf: Period during which the area is open daily / Average duration of a visit

Rf: 10 hours / 5 hours Rf: 2 visits / day

When the numerical values obtained are put in their respective places in the formula:

PCC: 270m x 1 visitor/m x 2 visits/day

PCC: 540 visits/day

The Real Carrying Capacity (RCC)

The climate factor is an important factor in terms of the recreational activities performed in the study area. Therefore, the 34-year (1980-2014) meteorological data about Çanakkale were obtained from the Directorate General for Meteorology of the Ministry of Forestry and Water Affairs, and the numerical values obtained from these data were used to calculate the correction factors. The RCC-related features of the area are as follows:

- ✓ Number of days when the temperature is greater than or equal to 25°C (annual mean): 121.9 days
- ✓ Daily hours of sunshine: 7.2 hours
- ✓ Period during which the sunshine is the most intensive: 4 hours (11 a.m.-3 p.m.)
- ✓ Number of days when precipitation is ≥ 0.1 mm (annual mean): 83.9 days
- ✓ Average duration of rainfall: 2 hours
- ✓ Mean number of stormy days (wind speed: 17.2 m/sec): 44.2 days
- ✓ Period during which the wind is effective: 2 hours

Some correction factors which limit visiting must be calculated to compute the RCC. Correction factors occur as a result of calculating the relationship between the limiting value

of the factors which prevent or limit visiting and the total value with the method of interpolation. The correction factors were determined as temperature, precipitation, and storm in BANP. The operations concerning the correction factors are presented in Table 3.

Table 3. Limiting Correction Factors

CORRECTION FACTORS
Correction Factor for Temperature
Cf_t : Vl / V_t x 100
V_l : 121.9 disturbing hot days x 4 disturbing hot hours = 487.6
V_t : 121.9 disturbing hot days x 7.2 sunny hours = 877.6
Cf_t : 487.6 / 877.6 x 100 = 55.5 (**55.5%**) limitation
Correction Factor for Precipitation
Cf_p : Vl / V_t x 100
Vl : 83.9 rainy days x 2 rainy hours = 167.8 hours/year
V_t : 5 visiting hours x 365 days = 1,825 hours / year
Cf_p : 167.8 / 1,825 x 100 = 9 (**9%**) limitation
Correction Factor for Storm
Cf_s : V_l / V_t x 100
V_l : 44.2 stormy days x 2 stormy hours = 88.4
V_t : 5 visiting hours x 365 days = 1,825 hours / year
Cf_s : 88.4 / 1,825 x 100 = 4 (**4%**) limitation

When the percent values found to calculate the RCC of the area are put in their respective places in the formula, it turns out that:

RCC = PCC x (100-Cf_f / 100) x (100-Cf_p / 100) x (100-Cf_s / 100)

PCC = 540 visits/day.

So,

RCC = 540 x (100-55.5 / 100) x (100-9 / 100) x (100-4 / 100)

RCC = 540 x (0.445) x (0. 91) x (0.96)

RCC = 210 visits/day

The Effective Carrying Capacity (ECC)

According to the information obtained from the Provincial Directorate for Nature Conservation and National Parks, the predicted number of staff members for BANP is 5 and the number of staff members available is 2. According to this information, the Management Capacity of the area can be calculated as follows:

MC = Number of Staff Members Available / Minimum Number of Staff Members Required x 100

MC = 2/5x100 = 40 (40%)

ECC = RCC x MC

ECC = 210 x 0.4

ECC = 84 visitors/day

As a result of the method of study, the ECC of BANP was found as 84 visits/day. The number of visitors that the area might accept per year was calculated as 30,660 (84 visitors/day x 365 days = 30,660 visitors/year).

5. DISCUSSION AND CONCLUSION

According to the data obtained from Çanakkale Provincial Directorate for Nature Conservation and National Parks of the Ministry of Forestry and Water Affairs, the number of visitors to BANP was 55,764 people in 2014; furthermore, again according to the data by the same institution, the number of visitors in a period of 5 months (June, July, August, September, and October) was 30,375 people in 2015. At this point, it is seen that the carrying capacity of the area was exceeded about twofold in 2014. On the other hand, the capacity limit was reached only in the period of 5 months in 2015. It is inevitable that the natural landscape features of the area (e.g. vegetation, animal stock, and water resources) will be negatively affected by this intensive use by visitors.

Diversification and acceleration of communication possibilities are quite essential for the development of tourism. However, this leads to a more intensive tourism movement in natural areas in particular. Although BANP is an area which is known and preferred by the people in the region, it is becoming an important destination point of Çanakkale nationwide upon the developing technology. This reveals that a conservation-based management plan should be drawn up rapidly for the sustainability of the resource assets of the area.

BANP also has various problems concerning the design of the area, along with the exceeding of its carrying capacity. In the examinations carried out in the area so as to reveal these problems, it was seen that the incoming vehicles mostly parked on the roadsides due to the lack of places in which an adequate number of parking lots could be constructed. Therefore, necessary arrangements (e.g. parking lot lines) should be made on the roadsides in terms of vehicle and pedestrian security. Furthermore, garbage elements, WC units, arbors and picnic tables were discovered to be inadequate. It was found out that children's playgrounds should be renewed with the tools and equipment suitable for the mental and physical development of children. For the security of individuals, regular maintenance and repair should be carried out on the wooden bridges that the visitors use when touring the area. A security point should be built at the entrance of the area. No arrangement for handicapped individuals is available within BANP. Regarding this matter, constructional solutions with accurate standards should be formed for handicapped individuals at all points where the topographical features of the area allow.

Fire (particularly due to the use of barbecues) is an important element of danger in the area. Barbecuing should be prevented outside the allowed areas, and necessary arrangements for control at the time of fire should be made at critical points. The local people in particular visit the study area largely for picnicking. By carrying out various activities for the local people, the area should be considered for other purposes, but not just with the concept of a "picnic area". Various activities which will enhance the awareness of individuals to recognize and protect the natural and cultural features of BANP should be performed. Moreover, introductory panels describing the natural and cultural features of the area and prepared individually for adults and children should be available. Regular sales units should be created in order for the local people to sell their own crops to visitors.

BANP is an area which should be protected with care in ecological terms particularly due to its rich vegetation. However, as Kuss and Graefe (1985) also state, one of the most

serious problems encountered in recreational resource areas by decision-makers about the area and by those who manage the area is the coincidence of the studies for the conservation of the natural ecosystem and the recreational uses. The study area is also confronted with similar problems. However, as Göktuğ et al. (2013) state by making a reference to Akten (2009), the goal adopted in the use of protected areas is to conserve natural and cultural assets and hand them down to future generations.

The natural and cultural landscape features of BANP, whose recreational carrying capacity is intended to be determined within the framework of this research, should be detected in detail with a large-scale study; it should be assessed in terms of different types of carrying capacity as well; and plan decisions for the future should be taken in light of the information to be obtained. As known, the contribution of protected natural areas to the tourism sector and hence to the development process is quite significant. Given this, the consciousness of the local people of the importance of this area and its close vicinity – which they also make use of in economic terms – as well as of the need to conserve them should be enhanced through various training activities. Adoption of the principle of participation when making plan decisions about protected areas will also enable the local people to have a more constructive attitude. Otherwise, the practices exceeding the self-renewability power of those natural features which are damaged by various uses in BANP and all similar protected natural areas will give rise to irreparable consequences.

There are many protected areas under different categories in Turkey, which houses very different natural landscape features not only on the local scale but also nationwide. These areas, in which tourism activities of various sizes and types are also ongoing, are under the responsibility of different institutions such as the Ministry of Forestry and Water Affairs, the Ministry of Environment and Urbanization, and the Ministry of Culture and Tourism. This causes differences in approaches in the planning performed. In addition, carrying capacity approaches and methods are not included in the plans on various scales drawn up by the relevant units of these ministries. Nevertheless, it should be acknowledged that the providing of sustainability in those protected natural areas particularly where there are intensive tourism activities depends on determining the carrying capacity of the area primarily in ecological terms and in every aspect.

In conclusion, protected natural areas are sensitive points for the whole world ecosystem. They are also striking and demanded destinations in terms of tourism because of the features they involve. Significant progress on sustainability will be achieved through the joint planning and policies that all relevant fields of science and institutions will draw up by considering the conservation-use balance in the context of handing these areas down to future generations.

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Dear Editor-in-Chief Assoc.Prof.Dr. Özlem Yayıntaş,

We are pleased for it was published the original research article entitled “Forensic medical aspect of right to life violation cases in ECHR decisions about Turkey from 1998 to 2002: revisiting the common errors in death investigations” in yours Journal of Scientific Perspectives, January 2018, Vol:2, Issue: 1: Doi: 10.26900/jsp.2018.05. However, there is a mistake about the authors' name. One of the authors’ names was no printed.

We, kindly ask you to review this mistake about the authors' name. We would like to want the editorial board of the journal approved the addition of the author's name and to publish an erratum article in Journal of Scientific Perspectives, July 2018.

Corrected Author list should be that: Esin Akgul Kalkan, Oğuz Polat.

Thank you for your interest and time.

With kind regards…

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