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Research Article

Investigation of the Activation Conditions of Kutahya-Unye Bentonite for Removal of Nickel from Waste Water

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Abstract

Any impurities above a certain concentration in water are harmful to the living spaces of living things. Therefore, the removal of pollutants in the water is very important in terms of maintaining the lives of living things. Nickel has an important place in metal coating due to its hardness, corrosion resistance and brilliance. Significant quantities of nickel are present in industrial and urban wastewater, particularly in steel enterprises and the electroplating industry waste waters. This study aims to investigate the effects of thermal and chemical activation conditions of Kutahya-Unye bentonite for removing nickel from wastewater. The bentonite samples were activated by two different methods: (i) thermal activation, (ii) acid activation. The operating range of the thermal activation studies was determined as 100, 300, 500, 700 ^{0}C. In the acid activation studies, the samples which were thermally activated, were entreated with 0.5 and 1 M HCl solutions. And, also acid activation was studied at different times to investigate the activation time on bentonite properties. The effects of temperature and acid treatment on calcium based-bentonite samples were investigated by Fourier Transform Infrared (FT-IR) between the region of 4000-400 cm^{-1}. It was observed that increasing the activation temperature has increased the nickel amount at the waste water. The optimal activation time for nickel removal from wastewater was determined to be 120 minutes, which resulted in the use of activation temperature 700 ^{0}C and 0.5 M HCl acid. It was concluded that if we can increase the adsorption capacity and applicability, Ca-bentonite may be a promising clay for the removal of nickel in the wastewater stream.

Keywords: Bentonite, Waste water, Nickel.

1. Introduction

Nowadays, very rapid advances in industry and the increase in population growth have led to the pollution of the atmosphere and water resources in our world. The fact that water is obligatory for human life and that it is used in every area of life and continuously, reveals the importance of water quality required for water. Any impurities above a certain concentration in water are harmful to the living spaces of living things. Therefore, the removal of pollutants in the water is very important in terms of maintaining the lives of living things [1]. Waste water from many industries, such as chemistry, mining and metallurgy, has become an increasingly serious problem for the environment. The substances, which are poisonous, can lead to diseases that cause harm to human health and even death if they are found in low concentrations in water [2].

There are various toxic heavy metals in the wastewater of the metal industry. Due to the frequent occurrence of these metals in wastewater, removal of heavy metals such as "Nickel" from aqueous solutions is necessary. Nickel has an important place in metal coating due to its hardness, corrosion resistance and brilliance. Especially iron, steel and copper are coated with nickel. It is used in the construction of instruments used in laboratories due to its resistance to chemical substances. Nickel is also a catalyst in many other organic reactions. Nickel, one of the heavy metals causing pollution in the water, constitutes 2 % by weight of the ground shell. Besides, the waters in the world contain about 3.4x10^7 kg Ni and the rivers carry 1.35x10^9 kg. year^{-1} nickel ion. Significant quantities of nickel (3.8x10^6 kg. year^{-1}) are present in industrial and urban wastewater, particularly in steel enterprises and the electroplating industry waste

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waters. While the level of nickel in uncontaminated water is generally in the range of 1-3 $g.L^{-1}$, this value can be increased to 10^{-15} $g.L^{-1}$ due to industrial wastewater. Nickel and its compounds have been identified as environmental factors that cause cancers in vivo. Heavy metals, such as nickel, must be removed from drain solutions due to their high presence in wastewater streams [3].

Nowadays, due to its accessibility, low cost and good intrinsic adsorption properties, clays find an increasing application in wastewater treatment as an adsorbent. Bentonite is one of the clay minerals containing montmorillonite. In the literature, the "natural" bentonite has not been found to be effective in the adsorption of contaminants [4] due to its hydrophilic surface properties. So, it has to be activated. Also, there are studies in the literature about removal of heavy metals in the water by using activated "sodium" bentonite as an adsorbent [5-8].

Acid activation is commonly used to improve the adsorption and catalytic properties of natural bentonites. The impurities, such as calcite and dolomite, are removed from the structure by the treatment of montmorillonite with inorganic acids, the exchangeable cations are replaced by hydrogen ions, and some of the Al ions in the tetrahedral layer dissolve some cations of Fe, Al and Mg in the octahedral layer. As a result, the acid activation process results in an increase in the pore diameters at the bentonite surface and in the surface area and adsorption capacity up to a certain amount of this application.

Although the changes in the structural properties of bentonites after acid activation have been studied extensively in the literature [9-14], the studies on nickel adsorption of these samples are very limited. Acid activation of bentonite with HCl or H_2SO_4 is an important process to increase the surface area and porosity of bentonite as well as to increase the absorptive properties [15]. For this reason, this study aimed to investigate the nickel adsorption properties of bentonites after thermal and acid modification.

2. Experimental

2.1. Materials

The bentonite samples used in the study was obtained from Unye Madencilik from the Ordu-Unye region of Turkey. It was crushed, grained and sieved to pass through <45 μm size. It was not active in its natural state. Table 1 shows the chemical composition of unactivated Unye Ca-bentonite. All the chemicals as hydrochloric acid and $NiCl_2.6H_2O$ were obtained from Merck and the chemicals used in the experiments were acquired as having high purity, and they were used directly without any purification. The Ni (II) stock solutions (200 mg/L) were prepared by dissolving a certain amount of the separately salts in double distilled water.

Table 1. Chemical composition of unactivated Ca-bentonite.

Compound	Chemical composition (%)
SiO_2	73.50
Al_2O_3	13.50
Fe_2O_2	0.76
TiO_2	0.13
CaO	1.72
MgO	1.67
K_2O	1.17
Na_2O	0.32
P_2O_4	0.02

2.2. Characterization

Fourier Transform Infrared Spectrophotometer (FTIR) (Perkin Elmer, Spectrum 100, USA) was used to understand the effect of activation of the all activated bentonites. The FTIR spectra were set in 4000-400 cm^{-1} and by using 4 cm-1 spectral resolution in the transmittance mode. The infra-red spectra of the both raw and modified bentonites were obtained by placing the samples, that are in the powder form, on the Diamond crystal to get FTIR spectra.

Rigaku, Miniflex 2 (Japan) analyzer was used to get X-Ray diffraction (XRD) analysis to investigate crystal structure of materials. 2θ values were scanned between 100 and 800 by using a 0.010/min step size and CuKα radiation (λ = 0.15418 nm) at 45kV/40mA.

2.3. Activation of Raw Bentonite

Natural bentonite was activated using thermal and acidic activation methods to improve adsorptive properties.

2.3.1. Thermal Activation

Bentonite samples each having a mass of 10 g were thermally activated by using muffle furnace and heating the samples to the desired temperature in a range of 100-700 ^{0}C. The temperature was raised steadily to the desired temperature within 5 minutes. The

samples were heated to the desired temperature and kept at this temperature for 30 to 120 minutes to investigate the effect of the activation time. The heated samples were then cooled and stored in a desiccator.

2.3.2. Acid Activation

0.5 M and 1 M HCl solutions were prepared for acid activation studies. At the beginning of the studies, 5 grams of the samples which were activated at 100, 300, 500, 700 ^{0}C and 30, 60, 90, 120 min. respectively, were weighted for acid activation studies. 100 ml of 0.5 M HCl solutions were taken in 4 beakers in a volume of 500 ml. Each sample was taken up in the acid solution and stirred for 15 minutes at a stirring speed of 500 rpm by using a magnetic stirrer. The samples were vacuum filtered and washed twice. The samples were dried at 100 ^{0}C for 24 hours, and they were bottled and stored in an air-tight environment. Then all the procedures were repeated using the acid solution at a concentration of 1 M HCl.

2.4. Experiments on Aqueous Media

Wastewater samples were synthetically prepared in laboratory environment. It was prepared a $2x10^{-2}$ M Ni^{+2} solution by using $NiCI_2.6H_2O$ as a stock solution. Water samples were prepared using this stock solution. Then, the absorbance values of all these solutions were confirmed by using a UV-spectrophotometer.

The capacity of activated Ca-bentonite samples to adsorb metal ions in aqueous media was investigated. The studies were carried out to remove Ni^{+2} from waste water. The activated bentonite samples were mixed with heavy metal containing wastewater samples in a magnetic stirrer for 2 hours at 200 rpm. UV-spectrophotometer was used to obtain the absorbance values of the receiving samples. Concentration values were calculated by drawing a calibration curve using the Lambert-Beer law.

3. Results and Discussion

3.1. Effect of Activation Temperature

To determine the effect of thermally activated Ca-bentonite samples on removing of nickel amount at waste water, the selected temperatures were 100, 300, 500 and 700 ^{0}C. Fig.1 shows the effect of activation temperature on removal efficiency of nickel by bentonite samples. In case of the thermally activated samples were used, the optimum nickel removal temperature for bentonite samples was determined as 700 ^{0}C. Increasing the temperature from 100 to 700 ^{0}C resulted in a decrease of almost half the amount of nickel in the wastewater.

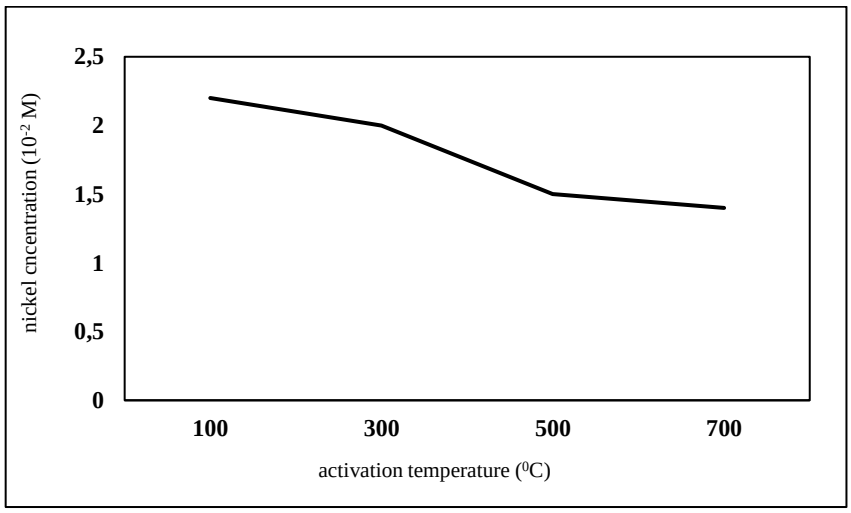

Figure 1. Effect of activation temperature on bentonite samples that were activated for 120 min.

As 700 ^{0}C has been recognized as optimum activation temperature, it was decided to use acid activation method on the thermally activated samples by using HCl at two different concentrations. Similar results have been obtained with both acid amounts (0.5 and 1 M) as seen at Fig.2.

The optimum activation conditions for nickel removal from wastewater was observed by using thermal activation at 700 ^{0}C followed by acid activation by using 0.5 and 1.0 M HCl. Acid activation caused a decrease from 1.4 x 10^{-2} M to 1.0 x 10^{-2} M by activating samples (thermally activated bentonites) with acids.

The FTIR spectra, obtained for the bentonites activated by the afore-mentioned methods, are also acquired. Figure 3 shows the FTIR spectra of the bentonites thermally activated at 100, 300, 500 and 700 ^{0}C during 120 min followed by acid activation by using 1 M HCl. These spectra help us understand the effect of activated samples on the chemical structure of bentonite.

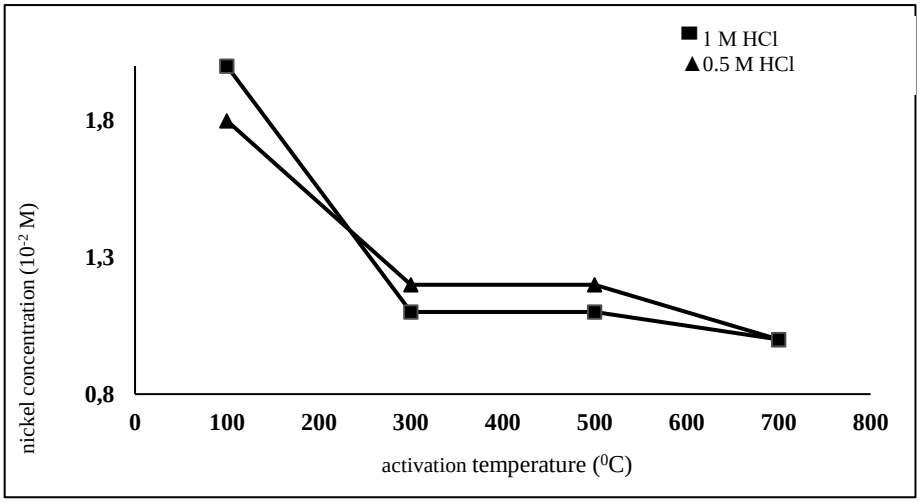

Figure 2. Effect of activation temperature and acid on bentonite samples that were activated for 120 min.

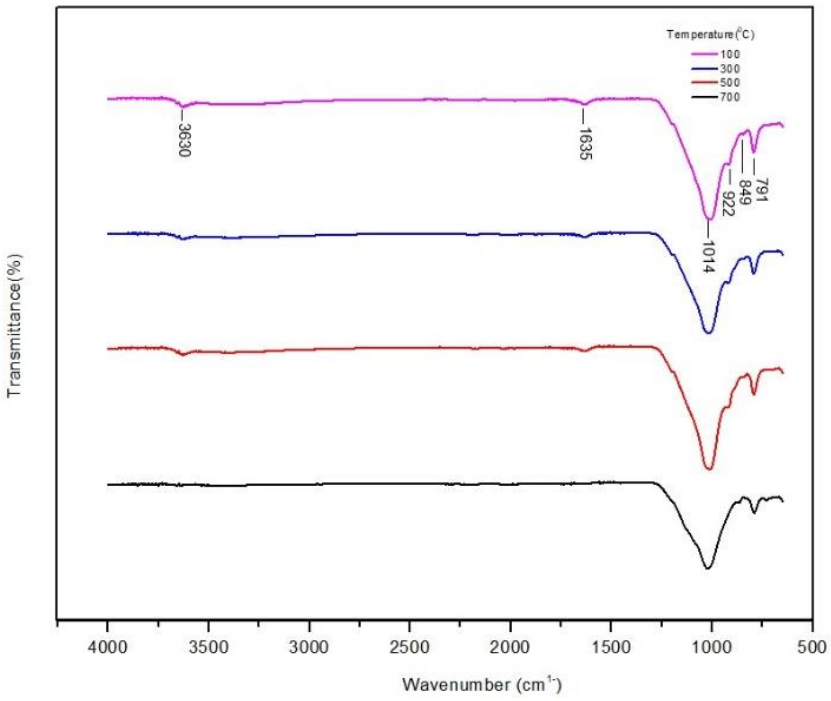

Figure 3. FTIR results of the samples that were activated at different temperatures during 120 min and 1 M HCl

The increase in activation temperature resulted with a decline at the intensity of peaks at 3630 cm^{-1}, that belongs to Al–OH–Al and Al–Mg–OH stretching vibrations, and at 1635 cm^{-1}, that belongs to H–O–H bending [5]. It was observed that the peak of Si-O-Si band remained unchanged at a wavelength of 1014 cm^{-1}. As the bentonite was heated to a temperature higher than 500 ^{0}C, the bands at 922 cm^{-1} disappeared. The other peaks remained constant. The results of FTIR exposed the effect of temperature rise to the disintegration of the structure at a constant acid concentration and reaction time.

FT-IR results show that there are three main absorption regions: The IR spectrum band at 3630 cm^{-1} shows the stretching vibrations of structural OH groups of montmorillonite. A peak, caused by Si-O stretching (in-plane) vibration of bentonite mineral, was observed at a wavelength of 1014 cm^{-1}. The absorption band, obtained at 1635 cm^{-1} wavelength, is referred to the OH dissolution of the water. Also, IR peak at 922 cm^{-1} was referred to Al–OH–Al. Quartz was also existing as specified by the bands at 790 cm^{-1} [10].

3.2. Effect of Thermal Activation Time

In order to investigate the effect of thermal activation time, both samples that were activated at 0.5 M and 1 M HCl solutions and at 700 ^{0}C, were used for nickel retention from waste water. Fig.4 shows the effect of thermal activation time on removal efficiency of nickel by activated bentonite samples.

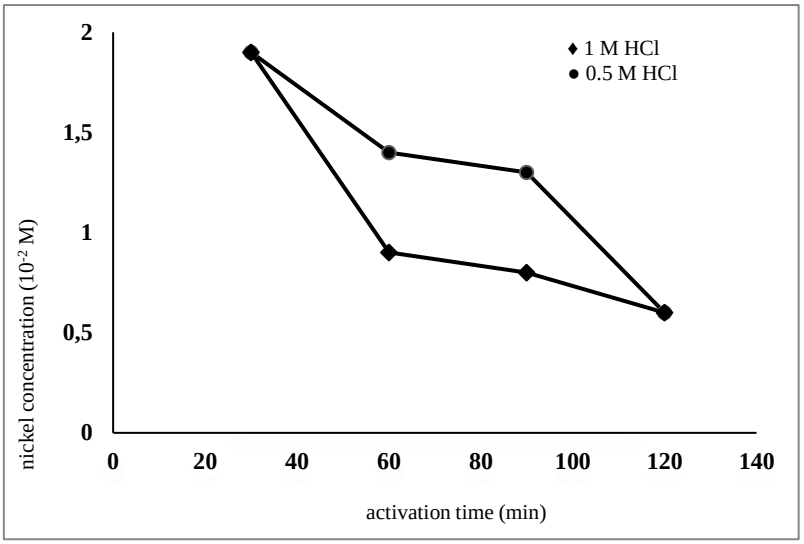

Figure 4. Effect of activation time with bentonite samples that was firstly activated at 700 ^{0}C

These results showed that the optimal activation time for bentonite samples by using both 0.5M and 1M HCI was found to be 120 min. The samples that were activated by using 1 M HCl solution ensured more nickel retention than the samples that were activated by using 0.5 M HCl. The samples which were activated at 0.5 M and 1 M HCl caused 0.6x10^{-2} M nickel concentration at 120 min.

Figure 5 shows the FTIR spectra of the bentonites thermally activated at 700 ^{0}C during 30, 60, 90 and 120 min and then used 1 M HCl for acid activation. The bands at 3630 and 1635 cm^{-1} were vanished by the time the bentonite samples were heated to 700 ^{0}C at all activation times. As it can be seen at the Figure 5, activation time has not show any effect on the structure of the bentonite. In figure 5, all samples give same spectra, there has been observed no signifcant difference. Figure 6 shows the XRD results of the of the sample that was activated at 700 ^{0}C and 1 M HCl.

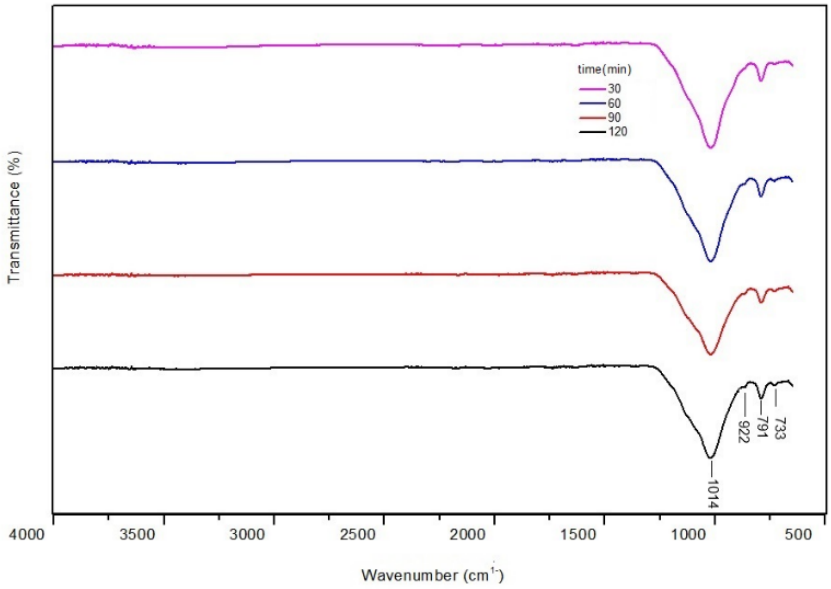

Figure 5. FTIR results of the samples that were activated at different times 700 ^{0}C and 1 M HCl

Montmorillonite and cristobalite structures have occured at high temperatures due to XRD graphs of the sample that was activated 700 ^{0}C and 1 M HCl. This result can be the main reason of the high nickel extincting from the waste water.

4. Conclusion and Recommendations

In this study, a new bentonite activation method (that can be found at Ordu/Turkey) was investigated for the aim of removing the nickel amount from wastewater streams. Bentonite clays were activated by simple thermal and acid activation under mild synthetic conditions. After the samples were activated, FT-IR analysis was carried out and the characteristics were examined.

The results deduced that the activation of Ca-bentonite thermally at 700 ^{0}C for 120 min and then with an acid (1 M HCl) increased the nickel adsorption capacity of raw bentonite seriously. Based on the results of this study, which was conducted due to the search for a low cost adsorbent, it can be said that the natural Ca-bentonite may be the ideal adsorbent for wastewater process with the development of the activation agents. In the future studies the activation of bentonite can be studied for more acid concentration and longer activation time values to identify the acid treatment effect.

Our test results, obtained as a result of both thermal and acidic activation conditions, executed that if we increase the adsorption capacity and applicability, Ordu/Ünye Ca-bentonite may be a promising clay for the removal of nickel in the wastewater stream.

References

Dinçer, I. 2002. Technical, environmental and exergetic aspects of hydrogen energy systems. International Journal of Hydrogen Energy 27(3), 265-285.

[1] Al-Shahrani, S.S. (2012). Treatment of wastewater contaminated with nickel using Khulays activated bentonite, *International Journal of Eng.& Techn.*, 12(4), 14-18.

[2] Ertuğral, F., Yakut, H., Tabar, E., Akkaya, R., Demirci, N., Zenginerler, Z. (2015). Measurements of Radon Content in the Thermal Waters in Sakarya, *Acta Physica Polonica A*, 128(2), 251-252.

[3] Madoni, P. (2000). The acute toxicity of nickel to freshwater ciliates, *Environmental Pollution*, (109), 53-59.

[4] Castrillo, N., Mercado, A., Volzone, C. (2015). Sorption Water By Modified Bentonite, *Procedia Materials Science*, (8), 391-396.

[5] Zong, P., Wu, X., Gou, J., Lei, X., Liu, D., Deng, H. (2015). Immobilization and recovery of uranium(VI) using Na-bentonite from aqueous medium: equilibrium, kinetics and thermodynamics studies, *Journal of Molecular Liquids*, (209), 358–366.

[6] Vhahangwele, M., Mugera, G.W. (2015). The potential of ball-milled South African bentonite clay for attenuation of heavy metals from acidic wastewaters: Simultaneous sorption of Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} ions, *Journal of Env. Chem. Eng.,* 3, 2416-2425.

[7] Yildiz, N., Koroglu, F., Calimli, A. (2006). HDTMA-bentonitinin sentez ve karakterizasyonu, *Journal of Eng&Arch.Fac. Eskişehir Osmangazi University,* 19(2), 21-34.

[8] Nigiz, F.U., Unlu, D., Hilmioglu, N., (2017). Carbon Black Loaded Composite Poly(Dimethyl Siloxane) Membrane Preparation and Application for Hazardous Chemical Removal from Water, *Acta Physica Polonica A*, (132), 693-696.

[9] Toor, M., Jin, B., Dai, S., Vimonses, V. (2015). Activating natural bentonite as a cost-effective adsorbent for removal of Congo-red in wastewater, *Journal of Ind. and Eng. Chem.,* 21, 653–661.

[10] Alver, B.E., Alver, O. (2012). Spectral characterization of non-clay minerals found in the clays (Central Anatolian-Turkey). *Spectrochimica Acta Part A,* 94, 331-333.

[11] Pawar, R.R., Lalhmunsiama, Bajaj, H.C., Lee, S.M. 2(016). Clay catalysed rapid valorization of glycerol towards cyclic acetals and ketals, *Journal of Industrial and Engineering Chemistry,* 34, 213–223.

[12] Maghni, A., Ghelamallah, M., Benghalem, A. (2017). Sorptive Removal of Methyl Green from Aqueous Solutions using Activated Bentonite, *Acta Physica Polonica A*, 132, 448-450.

[13] Bellifa, A., Makhlouf, M., Boumila, Zh.H. (2016). Comparative Study of the Adsorption of Methyl Orange by Bentonite and Activated Carbon, *Acta Physica Polonica A,* 132, 466-468.

[14] Tuğrul, B., Erentürk, S., Haciyakupoğlu, S., Karatepe, N., Altinsoy, N., Baydoğan, N., Baytaş, F., Büyük, B., Demir, E., Gedik, S. (2015). Kinetic and Thermodynamic Behavior of Selenium on Modified Bentonite and Activated Carbon using Radiotracer Technique, *Acta Physica Polonica A,* 128(2), 180-181.

[15] Nones, J., Riella, H.G., Trentin, A.G., Nones, J. (2015). Effects of bentonite on different cell types: A brief review, *App. Clay Sci.,* 105-106, 225-230.