Pamukkale Univ Muh Bilim Derg, 27(3), 368-377, 2021

Pamukkale Üniversitesi Mühendislik Bilimleri Dergisi

Pamukkale University Journal of Engineering Sciences

Removal of Zn (II) from water by magnetic hydroxyapatite nanocomposite

Manyetit-hidroksiapatit nanokompoziti ile sulardan Zn(II) iyonlarının gideriminin incelenmesi

Yağmur UYSAL[1*], *Ahmet CANBAKIŞ*[2]

[1]Department of Environmental Engineering, Engineering Faculty, Mersin University, Mersin, Turkey.
yuysal@mersin.edu.tr

[2]Graduate School of Natural and Applied Sciences, Kahramanmaras Sutcu Imam University, Kahramanmaras, Turkey.
ahmetcanbakis@windowslive.com

Received/Geliş Tarihi: 19.12.2019 Revision/Düzeltme Tarihi: 03.06.2020 doi: 10.5505/pajes.2020.94658
Accepted/Kabul Tarihi: 12.08.2020 Research Article/Araştırma Makalesi

Abstract

In this study, the capability of chemically synthesized hydroxyapatite-magnetite (HAp/Fe_3O_4-MHAp) nanocomposite for the sorption of Zn(II) ions was investigated. Magnetite-hydroxyapatite nanocomposite (MHAp) has been chosen as an adsorbent because of its excellent properties such as stability, low cost and effective sorption power. Adsorption process were tried to find the optimum conditions of the parameters for Zn(II) removal such as pH, concentrations of initial Zn(II) and adsorbent and reaction time. Nanocomposite properties were also characterized by using Fouirer Transform Infrared Spektrofotometre (FTIR), Scanning Electron Microscope (SEM) and Energy-dispersive X-ray Spectroscopy (EDX) techniques. Our results showed that the adsorption kinetic of Zn(II) using HAp/Fe_3O_4 composite fitted to the pseudo-second-order kinetic model. Calculations were carried out to determine which isotherm model the adsorption fits by using Langmuir, Freundlich, Tempkin, and Dubinin-Radushkevich (D-R) equations. Adsorption potential of MHAp nanocomposite was obtained 555.55 mg/g, and best removal value of 96% were determined at pH of 6.0, optimum adsorbent concentration of 6.25 g/L, in 25 mg/L Zn(II) concentration and optimum mixing time of 30 min. This study showed that the MHAp can be considered an effective adsorbent on the Zn(II) removal from wastewater.

Keywords: Adsorpsiyon, Atıksu, Çinko, Giderim, Hidroksiapatit, Manyetit.

Öz

Bu çalışmada, kimyasal olarak sentezlenen hidroksiapatit ve nano manyetit partiküllerinden manyetit-hidroksiapatit (HAp/Fe_3O_4-MHAp) nanokompozit malzemesi üretilmiş ve sulardan Zn(II) iyonlarının gideriminde adsorbent olarak kullanılmıştır. MHAp nanokompozit materyali düşük maliyet, kullanım ve üretim kolaylığı, yüksek stabilite ve etkili sorpsiyon kapasitesi gibi özelliklere sahip olduğu için seçilmiştir. Kesikli adsorpsiyon prosesine etki eden parametreler örneğin pH, başlangıç Zn(II) konsantrasyonu, adsorbent konsantrasyonu ve reaksiyon süresi için optimum değerlerin belirlenmesine yönelik deneyler gerçekleştirilmiştir. Elde edilen kompozit malzemenin özelliklerini belirlemek amacıyla Fourier Dönüşümlü Kızılötesi Spektroskopisi (FTIR), Taramalı Elektron Mikroskopu (SEM), Enerji yayılımlı X-Işını Analizi (EDX) kullanılmıştır. Adsorpsiyonun izoterm tipini belirlemek için Langmuir, Freundlich, Tempkin ve Dubinin-Radushkevich (D-R) izoterm modelleri denenmiş ve reaksiyonun zamanla değişimini tespit etmek amacıyla kinetic çalışmaları yürütülmüştür. Elde edilen sonuçlar, HAp/Fe_3O_4 kompozitinin sulardan Zn(II) iyonlarının gideriminde başarılı bir adsorbent olduğunu ve reaksiyon kinetiğinin Yalancı İkinci Dereceden Kinetik Modele uyduğunu göstermiştir. Optimum deneysel koşullarda (pH:6.0, 25 mg Zn(II)/L, 30 dk, 6.25 g/L MHAp) maksimum sorpsiyon kapasitesi 555.55 mg/g ve giderim verimi %96 olarak tespit edilmiştir.

Anahtar kelimeler: Adsorption, Hydroxyapatite, Magnetite, Removal, Wastewater, Zinc.

1 Introduction

Many industrial wastewater contains heavy metal ions in different concentrations, and they must be removed from the discharges before reach to the receiving environments. Zn(II) ions can be presented at high concentrations in wastewaters resulted from several industries such as pharmaceutical, pigment, paint, pesticide, cosmetic, and leachate of landfills [1],[2]. Various methods are used to treatment of these trace ions such as chemical, physical, and electrochemical treatment. The most important parameters before choosing the most appropriate treatment methods for an application should be economy and sustainability of the used technique when considering large volumes of wastewaters. Adsorption is a speed, effective and economical process to remove metal ions in wastewater treatment applications when adsorbents used in have high sorption capacities [3]. An adsorbent to be evaluated in the adsorption process should have a high surface area and reach to equilibrium state by holding pollutants in its surface as soon as possible [4]. Several adsorbents are used in the studies to remove various pollutants from wastewater such as organic polymeric and inorganic materials [5],[6]. In recent years, iron oxide based materials with economical costs and superparamagnetic properties are widely used as adsorbents, since they are non-toxic, easy to manufacture and environment friendly [7],[8]. Nano-adsorbents can be used in the environmental purification techniques because of their high sorption capacity within a short time [9].

Magnetite (Fe_3O_4) contains +2 and +3 loaded iron ions in its compound, and shows superparamagnetic properties. Magnetite nanoparticles are in the size of nanometers Magnetite nanoparticles have different nano sizes according to their different production methods and usage areas. [10]. The surface of Fe_3O_4 has hydroxyl groups [11] and this feature provide it effective metal removal by electrostatic attraction with positively charged metal cations.

*Corresponding author/Yazışılan Yazar

Polymers have been also used in the adsorption experiments because of their low costs, reusability, recoverability and performance [12]. Recently, magnetic hydroxyapatite (MA-HAP) composite has been used in the wastewater treatment studies as a new adsorbent material due to its high affinity to metal ions, low cost and eco-friendly characteristics [13]-[17]. Apatites are a natural source of phosphorus, and are found in the bone tissues of living things [18]. Hydroxyapatite (HAp-$Ca_5(PO4)_3(OH)$) is also an efficient adsorbent for heavy metals, paints and several pollutants in wastewater. [19]-[21]. In addition, preparation of HAp is easier for practical applications than other materials such as biochar, clays [22], and nanotubes and zeolites [23],[24]. There are many studies by using HAp to as an adsorbent material to remove several metal ions. For example, Smiciklas et al. [25] obtained quite high sorption potentials for Pb^{2+}, Cd^{2+} and Zn^{2+} as 676.1, 67.8 and 37.5 mg/g, respectively. Xia et al. [26] reported in their study for the Sr^{2+} removal efficiency from nuclear effluents with HAp as 98.94%. In addition, Sugiyama et al. [27] reported that heavy metal cations immobilized with phosphates of the HAp, and a dissolution-precipitation mechanism of metal phosphates contributed the metal removal [28].

In this present work, hydroxyapatite/magnetite (HAp/Fe_3O_4) was prepared to separate Zn(II) ions from water and to develop a new adsorbent for Zn(II) ions. The experimental factors affecting the process such as pH, reaction time, and concentration of Zn(II) were investigated. In order to find rate of the adsorption of Zn(II) ions, kinetic studies were also made, and kinetic and isotherm models that best describe the research results were explained.

2 Material and methods

2.1 Chemicals

All chemicals used in this research were analytical grade (Merck).

2.2 Preparation of MHAp

One of the methods used in synthesizing magnetite nanoparticles is co-precipitation method. In this method, Fe^{+2} and Fe^{+3} ions are precipitated as black precipitates in an inert environment such as nitrogen gas at high temperature. The sizes and shapes of nanoparticles produced vary with the effect of factors such as iron salt, pH, and ratio of +2 and +3 loaded iron ions in its structure [29],[30].

Magnetite nanoparticles were prepared according to Thanh et al. [31]. 23.3 g $FeCl_3.6H_2O$ and 8.6 g $FeCl_2.4H_2O$ were dissolved in 400 mL distilled water at 80 °C in nitrogen gas medium, and 30 mL of 25% NH_4OH solution was added. The mixture was allowed to cool at room temperature. Precipitate (Fe_3O_4) was separated with a magnet and washed with distilled water until the reach a neutral pH value. Magnetite-hydroxyapatite nanocomposites (MHAp) were prepared with the addition of Fe_3O_4 particles. 14.7 g of $CaCl_2$, 6.9 g of $NH_4H_2PO_4$ and 11.6 mL of C_2H_5OH were added to this precipitate and mixed for 30 minutes. After mixing, 10% NH_4OH was added to solution until the pH reached to 11.0. After the mixture was kept at room temperature, the precipitate in it was collected with magnet and washed with distilled water until the neutral pH. Finally, the mixture was dried in the oven at 50 °C and stored in the desiccator for use in experiments.

2.3 Adsorbent characterization

SEM analyses were used to identify synthesized MNP and MHAp particles. The characterization of the adsorbents was analyzed by FTIR, and XRD was used for elemental analysis. The pH measurements were made by pH-meter (Hanna HI 2211 pH/ORP). ICP-OES (Optima 2100-Perkin Elmer) was used to determine Zn(II) concentrations in water.

2.4 Experiments

Adsorption reactions were occurred at room temperature by using batch method. The pH adjustments were made using 0.1M HCl and 0.1M NaOH solutions. After adsorption, the adsorbent was removed from the water by precipitation with a magnet, and the solution was then centrifuged using a centrifuge. Zn(II) concentrations were measured to determine removal efficiencies.

The pH effect on Zn(II) removal was studied by mixing 6.25 g/L MHAp with 25 mg/L Zn(II) containing solutions. The pH was adjusted to pH:2.0-9.0 range. Because of the metal hydroxide precipitation occurred at pH>8.5, the maximum pH value was chosen as pH 9.0. Experiments were conducted at different HAp/Fe_3O_4 dosages of 1.25-12.5 g/L with constant pH (optimum) and 25 mg/L Zn(II) concentration to find optimum adsorbent concentration. Similarly, different Zn(II) concentrations of 10-100 mg/L, and different reaction times of 5-180 min experiments were conducted at to find optimal conditions. The kinetic behavior of Zn(II) adsorption on MHAp was studied by measuring its residual concentrations with time intervals.

The Zn(II) uptake capacity, q (mg/g) was examined based on the Eq. (1);

$$q = \frac{C_0 - C_e}{M} \times V \quad (1)$$

C_0 and C_e; Zn(II) concentrations at the beginning of the experiments and at equilibrium after adsorption (mg/L), V; solution volume (L), and M; mass of the MHAp (g/L).

2.5 Kinetic experiments

Kinetic behavior of a process refers to the time dependence of the mechanism. The most commonly used equations developed for the purpose of explaining the adsorption kinetics are pseudo first order, pseudo second order and intraparticle diffusion models. The pseudo first-order kinetic model introduced by Lagergren has been applied for the initial stages in which the adsorption process has not yet reached its equilibrium. This equation is as follows [32] (Eq. 2).

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (2)$$

After the integration, equation is converted the formula below (Eq. 3).

$$log(q_e - q_t) = log(q_e) - \frac{k_1}{2.303}t \quad (3)$$

In this equation q_e and q_t show the adsorbate amount at equilibrium and at any time of t (mg/g). k_1 is the rate constant (1/min) The equation of the pseudo second order kinetic model, which is in harmony with the speed control mechanism throughout the adsorption period, is as follows [33] (Eq. 4).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

k_2 is the rate constant(g/mg.min). The slope and intercept values were calculated to find the rate constant. This model provides to design and find size of the adsorption reactor.

Intraparticle diffusion model (Weber-Morris) was developed to define an inexplicable adsorption model with pseudo first and pseudo second order kinetic models [34] (Eq. 5)

$$q_e = k_p t^{0.5} \quad (5)$$

q_e is adsorbate amount at t time (mg/g); k_p is rate constant of model (mg/g 1/2); $t^{0.5}$: half time (min)

2.6 Adsorption isotherms

The data obtained from adsorption experiments were investigated by using five different isotherm models such as Langmuir (Eq. 6), Freundlich (Eq. 7), Dubinin Radushkevich (D-R) (Eq. 8, 9), Tempkin (Eq. 10, 11), and Scatchard (Eq. 12) models to determine the optimum isotherm model:

$$\frac{1}{q_e} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \quad (6)$$

$$Inq_e = InK_f + \frac{1}{nInC_e} \quad (7)$$

Where, q_e (mg/g) is MHAp capacity for Zn(II) adsorption, C_e is Zn(II) concentration in equilibrium (mg/L), q_m is maximum capacity of MHAp for Zn(II) adsorption (mg/g), K_f and b are the coefficients of Freundlich and Langmuir models, and n is the exponent of Freundlich model.

Isotherm equation for D-R shows the porosity of the adsorbent for intraparticle diffusion. The basis of the isotherm equation is based on the micropore volume distribution [35]. As the adsorption energy decreases, the capacity of the adsorbate to fill the pores on the adsorbent is increased.

$$\varepsilon = \mathrm{RTIn}(1 + \frac{1}{C_e}) \quad (8)$$

$$Inq_e = InX_m - K\varepsilon^2 \quad (9)$$

Where; X_m: maximum capacity of MHAp for Zn(II) adsorption (mg/g); K: isotherm constant; ε: Polanyi adsorption potential (kj/mol); R: Universal gas constant (8.314 j); T: Temperature (°K)

Interactions between the adsorbed substances are taken into account in the Tempkin isotherm. This isotherm was developed according to the adsorption enthalpy of all molecules in solution.

$$q_e = BInA_T + BInC_e \quad (10)$$

$$B = \frac{RT}{b_t} \quad (11)$$

b_t: Tempkin constant (J/mol); A_T: Equilibrium binding constant (L/g); T: Temperature (°K)

Scatchard isotherm can give more reliable results than Langmuir and Freundlich isotherm equations when it is used for the characterization of various materials, and characteristics of the adsorbate material. In other words, it is possible to comment on the suitability of the Langmuir and Freundlich models from the Scatchard curve derived for an adsorption process.

$$\frac{q_e}{C_e} = Q_s K_s - q_e K_s \quad (12)$$

where; Q_s: maximum capacity of MHAp for Zn(II) adsorption (mg/g), and K_s: Binding constant

3 Results and discussion

3.1 Characterizations of the adsorbents

The main factors affecting the efficiency of an adsorbent are its physical and chemical structure used in the process. Adsorbent surface area and its particle structure are also factors affecting the adsorption efficiency. Increasing surface area and decreasing particle size positively affect adsorption. In the present study, FTIR analyses were made to identify the adsorbents before and after the adsorption, and spectra were obtained as below (Figure 1).

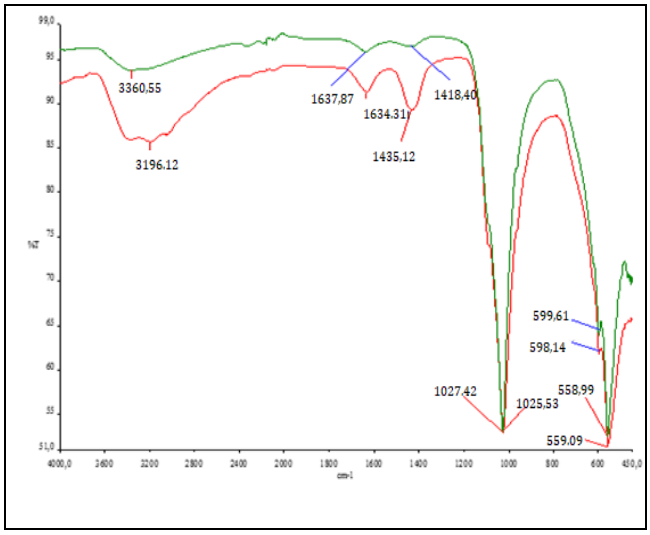
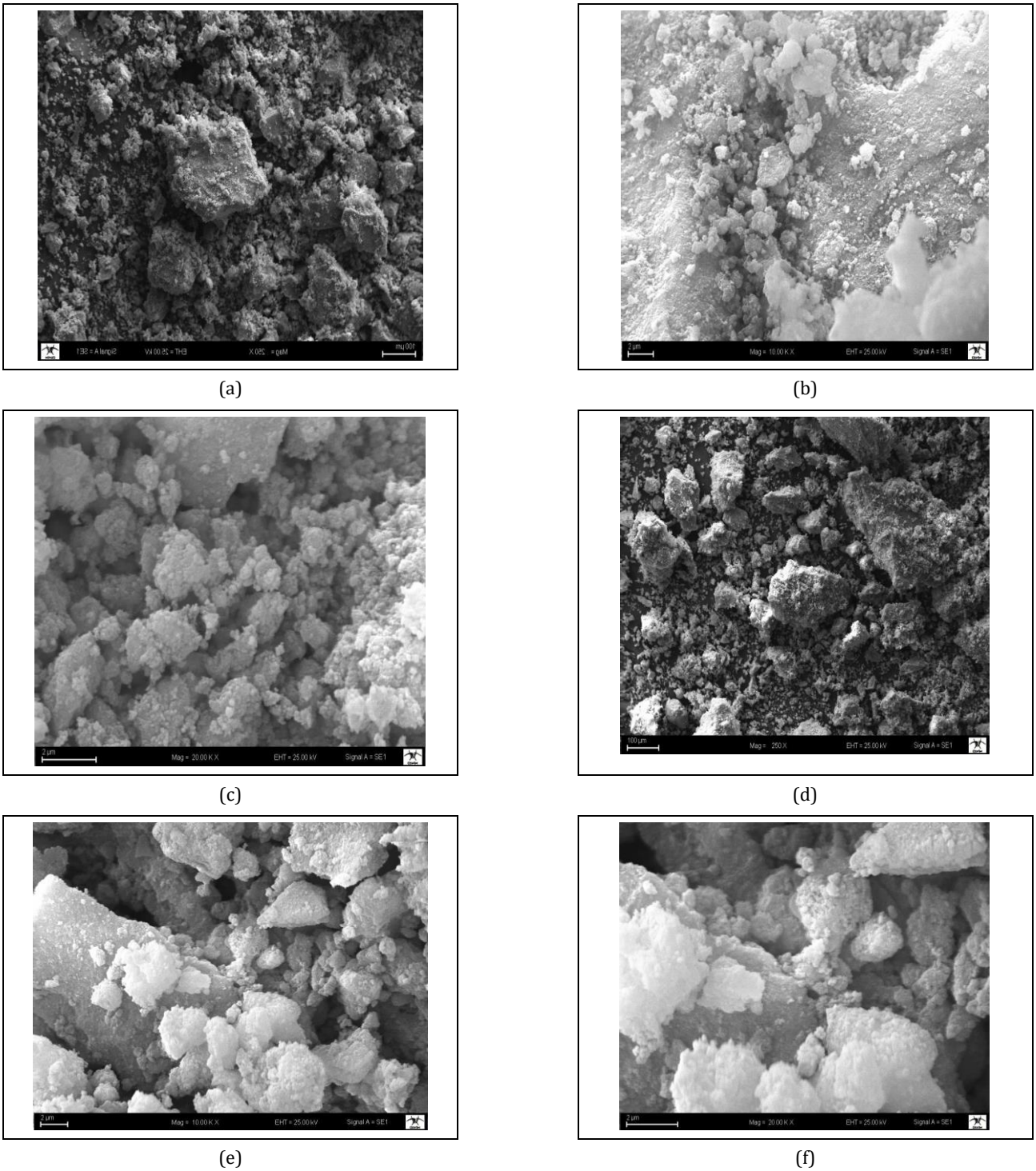


Figure 1. FTIR analyses before (*red line*) and after (*green line*) the adsorption process of the MHAp.

In the FTIR spectrum, the signaling of the oxygen-hydrogen (OH) bonds was observed in the 3196 cm^{-1} and 3360 cm^{-1} regions. The peaks of 1634-1637, and 1025-1027 cm^{-1} correspond the C=C and C-O stretching. The peak in the area of 1418~1435 cm^{-1} is considered to belong to the high phosphate stretch region. The peaks in the 598 cm^{-1} and in the 559 cm^{-1} regions are considered to the Fe-O stress zone and low phosphate stretch zone. The FTIR spectrum confirmed that the magnetite-hydroxyapatite nanocomposite contains oxygenated functional group. It can be said that all these groups affect heavy metal removal by acting as an existing adsorption site [36]. When the FTIR spectra after adsorption were examined, it was interpreted that peaks at 3196 cm^{-1}, 1634 cm^{-1} and 1435 cm^{-1} regions were relatively lost before adsorption, and zinc could be bounded to the bonds in these regions. SEM surface analyses of the adsorbent before and after the adsorption were occurred, and the following images were obtained (Figure 2). When the post-adsorption results are examined, it is possible to say that this porous and hollow structure is less than before and the adsorption is successful.



(a) (b) (c) (d) (e) (f)

Figure 2. SEM surface analyses of MHAp nanocomposite particles before (a), (b), (c) and after (d), (e), (f) the adsorption process.

The data obtained from the EDX elemental analyses of the adsorbent are as follows (Figure 3). Elemental analysis of MHAp showed that it contains 12.50% Calcium (Ca), 54.78% Oxygen (O), 9.74% Iron (Fe) and 8.96% Phosphorus (P) in its mass. After the adsorption process, its EDX analysis showed that it contains 33.14% Ca, 19.19% O, 28.50 Fe, 14.46% P, and 1.52% Zn(II) in its mass. In the EDX analysis after the adsorption, the presence of zinc appears in addition to the elements in the structure of the adsorbent, and it implies that Zn(II) adsorption took place on the MHAp surface successfully. Decrease in the calcium content of the adsorbent can be interpreted as replacement of calcium ions with zinc ions after the adsorption process.

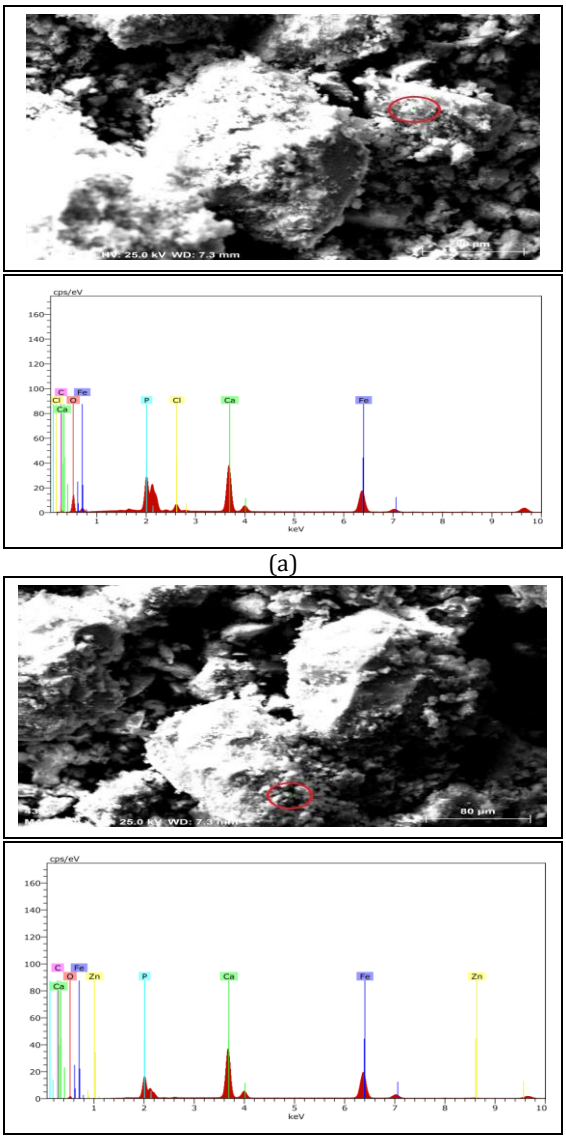


Figure 3. Elemental analysis of MHAp nanocomposite before. (a): and after the adsorption (b).

3.2 Experiments

3.2.1 The change of Zn(II) adsorption by MHAp with pH

pH is an important factor affecting the treatment efficiency of an adsorption process. Because pH value of a solution directly affects the behavior of metal ions in the dissolved state, and adsorbent surface charge. pH also affects the adsorption of other ions on the adsorbent surface because of hydrogen and hydroxide ions are strongly adsorbed. The pH effect on adsorption process was studied by adding MHAp nanoparticles (6.25 g/L) to the flasks containing 10 and 25 mg/L Zn(II) ions at different pH (2.0-9.0) for 60 minutes (Figure 4).

It is clearly seen from Figure 4 that the adsorption of Zn (II) on to MHAp increased with increasing pH, and this positive effect on adsorption revealed the pH had strong effect on the process. The best removal efficiencies were obtained at pH 6.0 and 9.0. However, in order to be close to neutral pH, easy to apply and to prevent precipitation of metal ions at high pH, pH 6.0 was selected as optimal pH, and other batch experiments were occurred at pH 6.0. Thanh et al. [31] used the magnetite-hydroxyapatite nanocomposite to remove copper and nickel ions. They tried different pH ranges of (3.0-5.0) and (3.0-7.0), in their experiments, and found the most suitable pH values as 5.0 and 7.0 for copper and nickel ions, respectively. Similarly, Nahid et al. [37] used magnetite amino nanoparticles as adsorbents for zinc ions removal. They carried out the experiments at different pH (2.0-7.0), initial zinc concentration of 5-20 mg/L, adsorbent dosages of 0.005-0.040 g/25 mL, adsorption time of 5-120 min, and temperature of 308-333 K range. They reported the optimum pH range for maximum Zn(II) removal was as 6.0-8.0.

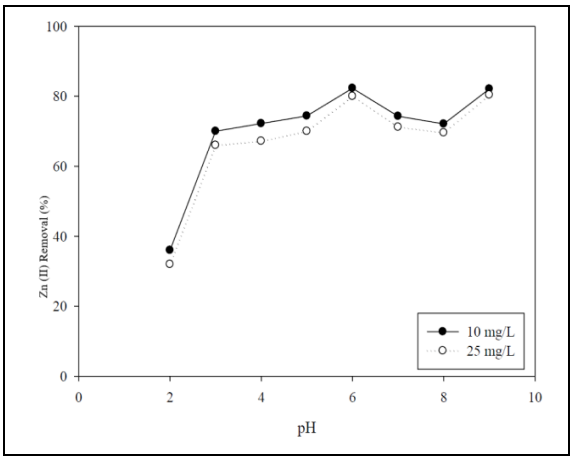


Figure 4. The change of Zn(II) removal by pH (MHAp: 6.25 g/L, t: 60 min).

The results of the study are consistent with the results of literature studies obtained for Zn(II) removal with different adsorbents such as clays [38]; geopolymeric powder of LD (Linz-Donawitz) [39] and hydrous MnO_2 [41]. Thanh et al [32] reported that Fe_3O_4 bound with hydroxyapatite to form a heterogeneous surface. The success of the magnetite-hydroxyapatite composite in adsorbing of metal ions has been mainly explained by 4 mechanisms: complexing on the surface, ion exchange, dissolution/precipitation and electrostatic attraction [40]. The both mechanisms of holding on to the surface and forming complexes are effective especially at high pHs (>4.0) [41].

3.2.2 The change of Zn(II) adsorption by MHAp with MHAp concentration

Adsorbate concentration changes the capacity of adsorbent and reaction rate. Since the amount of adsorbate per unit volume will vary at different concentrations, the amount of adsorbed adsorbate will also change. Thus, experiments were made by using the amount of adsorbents in the range of 1.25-12.5 g/L at pH 6.0 (Figure 5). As seen in Figure 5, Zn(II) removal efficiencies for both concentrations of 10 and 25 mg/L increased up to 6.25 g/L adsorbent concentration, and they did not change significantly after. Increasing of binding sites for Zn(II) with the presence of high adsorbent addition lead to increase of active sites on their surface, so this caused to increase of Zn(II) removal efficiencies. The maximum removal efficiency of 79.6% was obtained at the maximum MHAp concentration of 12.5 g/L while, this value was found as 78% for 6.25 g/L adsorbent concentration. For this reason, optimum MHAp dose was chosen as 6.25 g/L for next set of experiments.

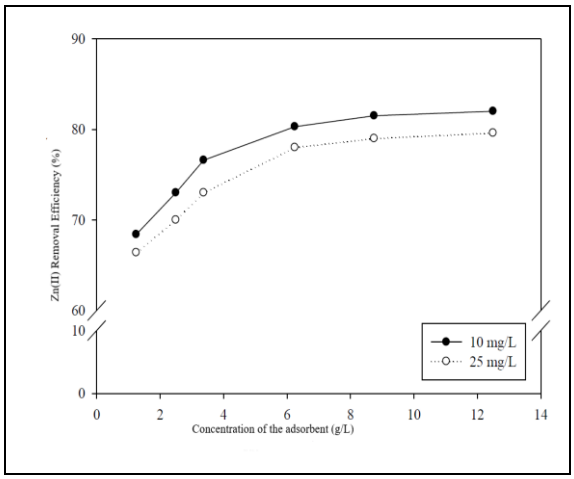


Figure 5. The change of Zn(II) removal by MHAp dosage (MHA: 6.25 g/L, t: 60 dk., pH:6.0).

Harja and Ciobanu [42] studied the removal of oxytetracycline (OTC) by hydroxyapatite from wastewater with adsorption method. They kept the adsorbent concentration at 0.1-5.0 g/L by fixing the experimental conditions constant (pH=8.0, OTC= 50 mg/L, time: 1 h, 20±1 °C) that affect the process. Removal efficiency of OTC increased with increasing adsorbent concentration, and maximum removal efficiency was achieved at 2 g/L adsorbent dose. The increase of the surface area increases the active areas on the surface of the hydroxyapatite, so the removal efficiency has also increased directly. They also reported out that main adsorption mechanism of OTC onto HAp is surface complexation. Periyasamy et al. [43] used hydroxyapatite alginate beads as adsorbents for Cr(VI) removal at pH range of 3.0-11.0, adsorbent dosages of 0.05-0.2 g/50 mL, Cr(VI) concentration of 100-200 mg/L, and reaction time of 10-100 min. They determined optimum adsorbent dose of 0.2 g/50 mL for adsorption process.

Wang et al. [44] used hydroxyapatite-biochar nanocomposite (HAP-BC) adsorbent to remove lead, copper and zinc ions in single and ternary metal system. Adsorption experiments were conducted on different experimental conditions such as pH (2.0-6.0), initial metal ion concentrations (25-1000 mg/L), time (10-1440 min), and HAP-BC concentration (1000 mg/L). Since the adsorbent surface is charged positively at low pH, the formation of electrostatic repulsion forces between heavy metal ions negatively affected the adsorption efficiency. When pH increased, adsorption efficiency increased by high electrostatic attraction forces.

3.2.3 The change of Zn(II) adsorption by concentration and time

Industrial wastewater can contain more than one heavy metal ion at different concentrations. Therefore, pre-process concentrations of heavy metal ions are an important factor directly affecting adsorption efficiency. Zinc concentration effect (10-100 mg/L) on adsorption was determined by keeping the other parameters constant (pH=6.0, MHAp: 6.25 g/L, t: 60 min, T: 22±2°C). The adsorbed amount of Zn(II) decreased with increasing zinc ion concentration because of the solution's adsorbent dose was constant (Figure 6). It was decided to choose optimum Zn(II) concentration as 25 mg/L in order to reach high removal efficiency of 82%.

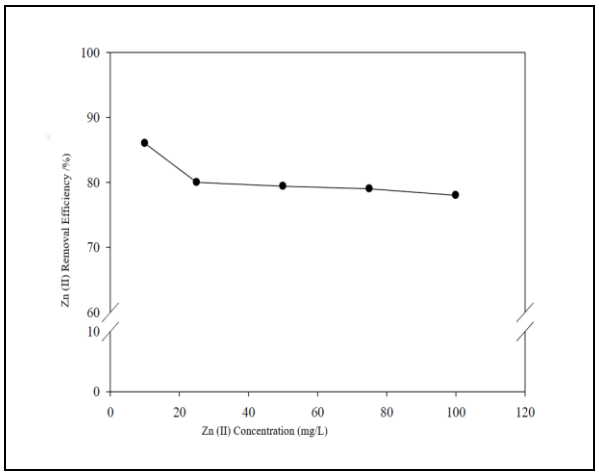


Figure 6. The change of Zn(II) removal by initial Zn(II) concentration (MHAp: 6.25 g/L, t: 60 dk., pH:6.0, 10-100 mg/L).

In the adsorption process, a certain time is required to adhere the adsorbate to the adsorbent surface. Thus, one of the most important criteria to be determined in the applications of the adsorption is to determine the optimum contact time. Adsorption efficiency will increase with increasing of the contact time up to a certain period, and it will reach to stable value after the reach to equilibrium. In order to find contact time effect on the process, experimental runs were conducted at pH 6.0, adsorbent dose of 6.25 g/L, and in 10-100 mgZn(II)/L for 5-180 min. According to Figure 7, the removal efficiency reached the maximum in the first 30 minutes, then a reduction was occurred, and did not change over time after from 60 min. Batch experiments were carried out for 60 min, where the adsorption forces were determined to be time required to reach equilibrium.

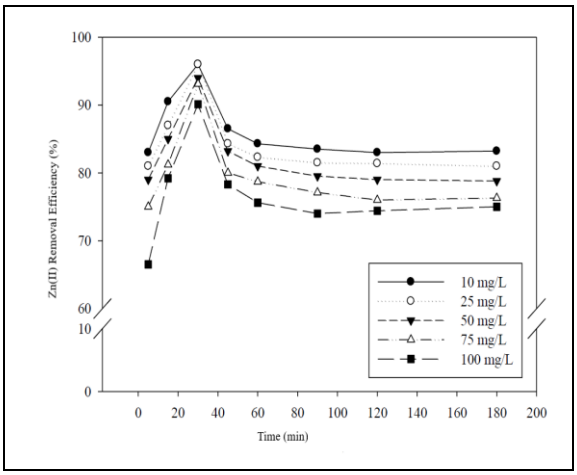
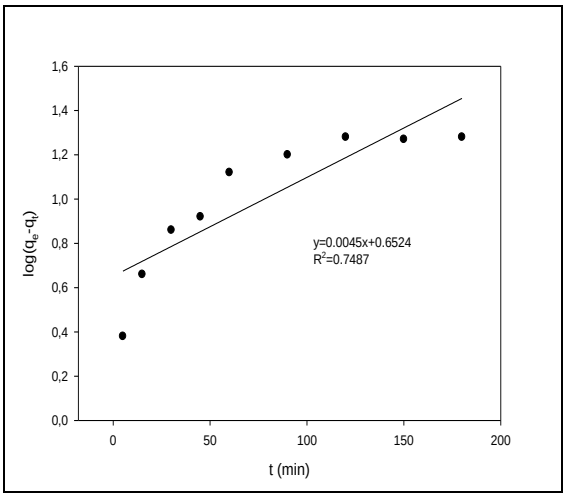


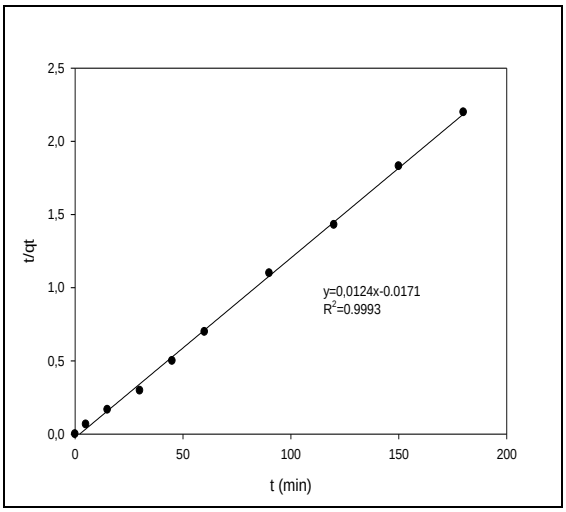
Figure 7. The change of Zn(II) removal by reaction time (MHAp: 6.25 g/L, pH: 6.0, 10-100 mgZn(II)/L, t: 10-180 min).

3.3 Adsorption kinetics

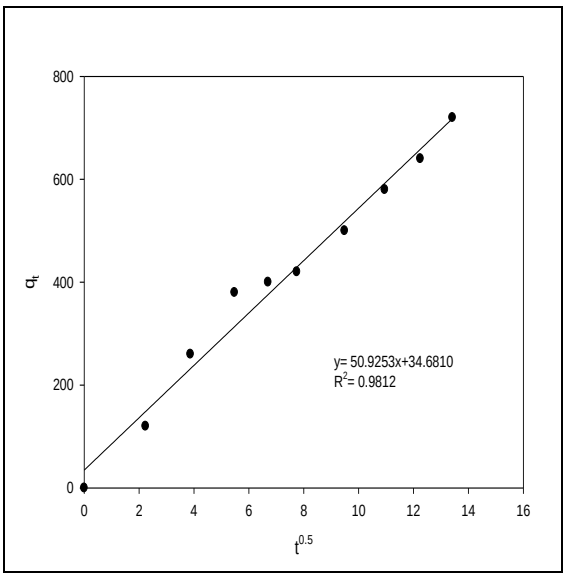
In order to find kinetic behavior of Zn(II) adsorption by MHAp, different kinetic models were tried on the experimental results (Figure 8).



(a)



(b)



(c)

Figure 8. The pseudo first order. (a): Pseudo-second order. (b): and intraparticle diffusion. (c): Models for Zn(II) removal by MHAp.

Correlation coefficients (R^2) were calculated, and the parameters of each model were summarized to see which of the examined models explain the kinetic results of our study better (Table 1).

Table 1. Kinetic behavior of MHAp for Zn(II) removal (pH 6.0, 6.25 gMHAp/L, 25 mg Zn(II)/L, 22±2 °C).

Kinetic models	Parameters	Value
Pseudo-first order kinetic	q_e (mg/g)	4.491
	k_1 (min^{-1})	0.010
	R^2	0.749
	SS	9.750
	MS	1.083
	P	0.0026
Pseudo-second order kinetic	q_e (mg/g)	58.479
	k_1 (g/mg.min)	80.645
	R^2	0.999
	SS	12.287
	MS	1.228
	P	<0.0001
Intraparticle diffusion	q_e (mg/g)	34.681
	k_p (mg/g·$min^{0.5}$)	50.925
	R^2	0.981
	SS	2077200
	MS	207720
	P	<0.0001

SS: Sum of Squares; MS: Mean Squares; Results are statistically significant ($p<0.05$).

The pseudo second order equation with R^2 value of 0.9995 was found to best kinetic equation to describe Zn(II) the adsorption kinetic on nanohydroxyapatite powders followed by the intraparticle (pore) diffusion model (R^2: 0.9812). This result shows that adsorption does not only occur due to the mechanism of holding or complexing on the surface, but also zinc ions are diffused into the micro and nano pores of MHAp. The obtained results revealed that Zn (II) ions diffuse to the surface of MHAp, and then a two-stage adsorption takes place in the form of diffusion into the particle of the adsorbent [42].

3.4 Adsorption isotherms

Chemical structures of the adsorbents and their surface are important factors affecting the adsorption reactions and isotherm behaviors. The adsorption reaction continues until the capacity of the solid surface used reaches the equilibrium. Adsorbent adsorbs pollutants in water until all surface areas are filled. At the maximum adsorption point, the amount of adsorbate remaining in the solution does not change. Adsorption isotherms define the relationship between adsorbent and adsorbate. Process feasibility can be assessed for

a given application for example the most suitable adsorbent can be selected and the adsorbent dosage requirements can be determined by using experimental isotherms. The regression coefficients of the four isotherm models used, and the parameters required to show the which isotherm is compatible are given in Table 2.

Table 2. Isotherms and their calculated parameters used in the Zn(II) adsorption on MHAp.

Isotherms	Parameters		
Langmuir	R^2	b	q_m
	0.998	0.041	555.550
Freundlich	R^2	K_f	n
	0.999	23.33	1.198
Tempkin	R^2	B	b_t
	0.9091	100.480	0.678
Scatchard	R^2	K_s	Q_s
	0.840	0.0255	828.039
Dubinin Radushkevich	R^2	K	X_m
	0.8028	-1x10^{-6}	199.930

The correlation coefficients (R^2) for Freundlich and Langmuir models were found to be higher than the correlation coefficient values for the other models. Based on the R^2 values, it was revealed that Freundlich model defines the adsorption of zinc ions by MHAp very well and show the adsorption occurs in the form of multiple layers. Especially the value of 1/n close to 1 showed that adsorption occurs with a homogeneous distribution. In addition, Langmuir model with high R^2 value of 0.9978 has defined the adsorption process very well. The maximum adsorption capacity by unit adsorbent mass was calculated as 555.55 mg/g for Zn(II) from Langmuir model.

4 Conclusions

In this study, Zn (II) adsorption of MHAp from water was investigated as an innovative adsorbent material. In this study, the success of magnetic MHAp, which prepared with magnetite and hydroxyapatite powders by coprecipitation method on the adsorption, and the suitability of the obtained data to kinetic and isotherm models were studied. Adsorption reactions were dependent on pH, adsorbent dosage, and contact time. The adsorption process occurred fast and reached its maximum in the first 30 min with 6.25 g/L MHAp for all studied Zn(II) concentrations of 10-100 mg/L. In the first 30 min, it reached to maximum removal efficiencies of >90%. Therefore, MHAp has shown excellent adsorption performance for Zn(II) as an innovative magnetic adsorbent with a quite high q_m value of 555.55 mg/g. The kinetic behavior of MHAp adapted to pseudo-second order kinetic and pore diffusion models very well, and isotherm results could be explained by Freundlich and Langmuir isotherms. Results showed that magnetite-hydroxyapatite nanocomposite could be a new adsorbent for zinc removal from wastewater in the treatment applications.

5 Author contribution statements

In this study, *Yağmur UYSAL* is responsible for the formation of the main idea of the research, its design, the literature review, the materials used, the interpretation of the results and the writing of the article; *Ahmet CANBAKIŞ* contributed to the analyzes, obtaining the experimental results and drawing the graphics.

6 Ethics committee approval and conflict of interest statement

There is no need to obtain permission from the ethics committee for the prepared article, and there is no conflict of interest with any person / institution in the article.

7 References

[1] Fan HJ, Shu HY, Yang HS, Chen WC. "Characteristics of Landfill Leachates in Central". *Taiwan. Science of the Total Environment,* 361 (1-3), 25-37, 2006.

[2] Bhattacharya AK, Mandal SN, Das SK. "Adsorption of Zn(II) from aqueous solution by using different adsorbents". *Chemical Enginering Journal*, 123(1-2), 43-51, 2006.

[3] Rashed MN. *Adsorption Technique for the Removal of Organic Pollutants From Water and Wastewater*. Editor: Mohamed Rageeb Nashed. Organic Pollutants-Monitoring, Risk and Treatment. 167-194, Intech Open, 2013.

[4] Gupta VK. "Application of low-cost adsorbents for dye removal- a review". *Journal of Environmental Management,* 90(8), 2313-2342, 2009.

[5] Crini G. "Non-conventional low-cost adsorbents for dye removal: a review". *Bioresource Technology,* 97(9), 1061-1085, 2006.

[6] Gong JL, Wang B, Zeng GM, Yang CP, Niu CG, Niu QY, Zhou WJ, Liang Y. "Removal of cationic dyes from aqueous solution using magnetic multi-wall carbon nanotube nanocomposite as adsorbent". *Journal of Hazard Mater*, 164(2-3), 1517-1522, 2009.

[7] Liu G, Gao J, Ai H, Chen X. "Applications and potential toxicity of magnetic iron oxide nanoparticles". *Small,* 9(9-10), 1533-1545, 2013.

[8] Bao S, Tang L, Li K, Ning P, Peng J, Guo H, Zhu T, Liu Y "Highly selective removal of Zn(II) ion from hot-dip galvanizing pickling waste with amino-functionalized Fe_3O_4@SiO_2 magnetic nano-adsorbent". *Journal of Colloid and Interface Science,* 462, 235-242, 2016.

[9] Karami H. "Heavy metal removal from water by magnetite nanorods". *Chemical Engineering Journal,* 219, 209-216, 2013.

[10] Nagpal M, Kakkar R. "Use of metal oxides for the adsorptive removal of toxic organic pollutants". *Separation and Purification Technology,* 211, 522-539, 2019.

[11] Su C. "Environmental implications and applications of engineered nanoscale magnetite and its hybrid nanocomposites: A review of recent literature". *Journal of Hazardous Materials*, 322(Part A), 48-84, 2017.

[12] Zhou Y, Fu S, Zhang L, Zhan H, Levit MV. "Use of carboxylated cellulose nanofibrils-filled magnetic chitosan hydrogel beads as adsorbents for Pb (II)". *Carbohydrate Polymers,* 101, 75-82, 2014.

[13] Lu AH, Salabas EL, Schüth F. "Magnetic nanoparticles: synthesis, protection, functionalization, and application". *Angewandte Chemie International Edition*, 46, 1222-1244, 2007.

[14] Mondal S, Manivasagan P, Bharathiraja S, Moorthy MS, Kim HH, Seo H, Lee KD, Oh J. "Magnetic hydroxyapatite: a promising multifunctional platform for nanomedicine application". *International Journal of Nanomedicine*, 12, 8389-8410, 2017.

[15] Dong L, Zhu Z, Qiu Y, Zhao J. "Removal of lead from aqueous solution by hydroxyapatite/magnetite composite adsorbent". *Chemical Engineering Journal,* 165(3), 827-834, 2010.

[16] Akmal M, Khalid FA, Hussain MA. "Interfacial diffusion reaction and mechanical characterization of 316L stainless steel-hydroxyapatite functionally graded materials for joint prostheses". *Ceramics International,* 41(10), 14458-14467, 2015.

[17] Akmal M, Raza A, Khan MM, Khan MI, Hussain MA. "Effect of nanohydroxyapatite reinforcement in mechanically alloyed NiTi composites for biomedical implant". *Materials Science and Engineering: C*, 68, 30-36, 2016.

[18] Oelkers EH, Valsami-Jones E. "Phosphate mineral reactivity and global sustainability". *Elements,* 4(2), 83-87, 2008.

[19] Ciobanu G, Ignat D, Carja G, Luca C. "Hydroxyapatite/polyurethane composite membranes for lead ions removal". *Environmental Engineering and Management,* 8(6), 1347-1350, 2009.

[20] Nishiyama Y, Hanafusa T, Yamashita J, Yamamoto Y, Ono T. "Adsorption and removal of strontium in aqueous solution by synthetic hydroxyapatite". *Journal of Radioanalytical and Nuclear Chemistry*, 307, 1279-1285, 2016

[21] Wang S, Liu H, Liu W, Zuo Q. "Effect of low-molecular-weight organic acids on nano-hydroxyapatite adsorption of cadmium and lead". *Journal of Biomaterials and Tissue Engineering,* 6(6), 433-439, 2016.

[22] Yoo JI, Shinagawa T, Wood JP, Linak WP, Santoianni DA, King CJ, Wendt JOL. "High-temperature sorption of cesium and strontium on dispersed kaolinite powders". *Environmental Science & Technology,* 39(13), 5087-5094, 2005.

[23] Wen T, Wu X, Liu M, Xing Z, Wang X, Xu AW. "Efficient capture of strontium from aqueous solutions using graphene oxide-hydroxyapatite nanocomposites". *Dalton Transactions,* 43(20), 7464-7472, 2014.

[24] Yang D, Sarina S, Zhu H, Liu H, Zheng Z, Xie M, Smith SV, Komarneni S. "Capture of radioactive cesium and iodide ions from water by using titanate nanofibers and nanotubes". *Angewandte Chemie International Edition,* 50(45), 10594-10598, 2011.

[25] Smiciklas I, Dimovic S, Plecas I, Mitric M. "Removal of Co^{2+} from aqueous solutions by hydroxyapatite". *Water Research,* 40(12), 2267-2274, 2006.

[26] Xia X, Shen J, Cao F, Wang C, Tang M, Zhang Q, Wei S. "A facile synthesis of hydroxyapatite for effective removal strontium ion". *Journal of Hazardous Materials,* 364, 326-335, 2019.

[27] Sugiyama S, Ichii T, Masayoshi F, Kawashiro K, Tomida T, Shigemoto N, Hayashi H. "Heavy metal immobilization in aqueous solution using calcium phosphate and calcium hydrogen phosphates". *Journal of Colloid and Interface Science,* 259(2), 408-410, 2003.

[28] Venkatesan S, Hassan M, Ryu H. "Adsorption and immobilization of radioactive ionic-corrosionproducts using magnetic hydroxyapatite and cold-sintering for nuclear waste management applications". *Journal of Nuclear Materials,* 514, 40-49, 2019.

[29] Lee J, Isobe T, Senna M. "Magnetic properties of ultrafine magnetite particles and their slurries prepared via in-situ precipitation". *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 109, 121-127, 1996.

[30] Kim JH, Kim SM, Kim YI. "Properties of magnetic nanoparticles prepared by co-precipitation". *Journal of Nanoscience and Nanotechnology,* 14(11), 8739-8744, 2014.

[31] Thanh DN, Novak P, Vejpravova J, Vu HN, Lederer J, Munshi T. "Removal of copper and nickel from water using nanocomposite of magnetic hydroxyapatite nanorods". *Journal of Magnetism and Magnetic Materials,* 456, 451-460, 2018.

[32] Lagergren S. "About the theory of so-called adsorption of soluble substance". *Kung Sven Veten. Hand*, 24(4), 1-39, 1898.

[33] Ho YS, Mckay G. "Pseudo-second order model for sorption processes". *Process Biochemistry*, 34(5), 451-465, 1999.

[34] Weber Jr WJ, Morriss JC. "Kinetics of adsorption on carbon from solution". *Journal of the Sanitary Engineering Division,* 89(2), 31-60, 1963.

[35] Jiun-Horng T, Hsiu-Mei C, Guan-Yinag H, Hung-Lung C. "Adsorption characteristics of acetone, chloroform and acetonitrile on sludge-derived adsorbent, commercial granular activated carbon and activated carbon fibers". *Journal of Hazardous Materials*, 154(1-3), 1183-1191, 2008.

[36] Yaoguang W, Lihua H, Guangya Z, Tao Y, Liangguo Y, Qin W, Bin D. "Removal of Pb(II) and methylene blue from aqueous solution by magnetic hydroxyapatite-immobilized oxidized multi-walled carbon nanotubes". *Journal of Colloid and Interface Science,* 494, 380-388, 2017.

[37] Nahid G, Maryam G, Saleh M, Paris G, Njud SA, Vinod KG, Agarwal S, Burakova IV, Tkachev AV. "Zn (II) removal by amino-functionalized magnetic nanoparticles: kinetics, isotherm, and thermodynamic aspects of adsorption". *Journal of Industrial and Engineering Chemistry*, 62, 302-310, 2018.

[38] Saida MG, Frini-Srasra N. "A comparison of single and mixed pillared clays for zinc and chromium cations removal". *Applied Clay Science,* 158, 150-157, 2018.

[39] Chayan S, Jayanta K, Basu A, Nath S. "Synthesis of mesoporous geopolymeric powder from LD slag as superior adsorbent for zinc (II) removal". *Advanced Powder Technology,* 29(5), 1142-1152, 2018.

[40] Kanungo SB, Tripathy SS, Rajeev. "Adsorption of Co, Ni, Cu, and Zn on hydrous manganese dioxide from complex electrolyte solutions resembling sea water in major ion content". *Journal of Colloid and Interface Science,* 269(1), 1-10, 2004.

[41] Valsami-Jones E, Ragnarsdottir KV, Putnis A, Bosbach D, Kemp AJ, Cressey G. "The dissolution of apatite in the presence of aqueous metal cations at pH 2-7". *Chemical Geology,* 151(1-4), 215-233, 1998.

[42] Harja M, Ciobanu G. "Studies on Adsorption of oxytetracycline from aqueous solutions onto hydroxyapatite". *Science of the Total Environment*, 628-629, 36-43, 2018.

[43] Periyasamy S, Gopalakannan V, Viswanathan N. "Hydrothermal assisted magnetic nano-hydroxyapatite encapsulated alginate beads for efficient Cr(VI) uptake from water". *Journal of Environmental Chemical Engineering,* 6(1), 1443-1454, 2018.

[44] Wang Y, Liu Y, Lu H, Yang R, Yang S. "Competitive adsorption of Pb(II), Cu(II), and Zn(II) ions ontohydroxyapatite-biochar nanocomposite in aqueous solutions". *Journal of Solid State Chemistry,* 261, 53-61, 2018.