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SYNTHESIS OF HYDROXYAPATITE FROM EUROPEAN SEA BASS (*DICENTRARCHUS LABRAX*) SCALES AND INVESTIGATION OF ITS USABILITY IN Pb(II) REMOVAL FROM WATERS

ATIK BALIK PULLARINDAN HIDROKSİAPATİT SENTEZİ VE SULARDAN Pb(II) GİDERİMİNDE KULLANILABİLİRLİĞİNİN ARAŞTIRILMASI

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ABSTRACT

In this study, low-cost and eco-friendly hydroxyapatite (FS-HAp) particles were obtained from the raw fish scales of European Seabass (*Dicentrarchus labrax*), and used as adsorbent material to remove Pb(II) ions from solutions. For this purpose, experiments were carried out in the aqueous solutions prepared at different Pb(II) concentrations to determine optimum pH, adsorbent concentration, reaction time and initial Pb(II) concentration. Optimum removal conditions for Pb(II) adsorption onto FS-HAp were determined as pH 4.0, adsorbent concentration of 7.5 g/L, reaction time of 60 min, and initial Pb(II) concentration of 50 mg/L. Under these experimental conditions, the maximum Pb(II) removal was obtained as 97%. According to results of the study, hydroxyapatite obtained from fish scales was found to be highly efficient material to remove Pb(II) ions from water by adsorption method in order to reach high efficiency values when compared with many adsorbent materials.

Keywords: Fish scales, european seabass, hydroxyapatite, lead, removal, wastewater

ÖZET

Bu çalışmada, Avrupa Deniz Levreği (*Dicentrarchus labrax*) pullarından düşük maliyetli ve çevre dostu hidroksiapatit (BP-HAp) partikülleri elde edilmiş ve su ortamından kurşun-Pb(II) iyonlarını uzaklaştırmak için adsorban malzeme olarak kullanılmıştır. Bu amaçla, optimum pH, adsorban konsantrasyonu, reaksiyon süresi ve başlangıç Pb(II) konsantrasyonunu belirlemek için farklı Pb(II) konsantrasyonlarında hazırlanan sulu çözeltilerde deneyler yapılmıştır. BP-HAp üzerine Pb(II) adsorpsiyonu için optimum giderim koşulları pH 4.0, adsorban konsantrasyonu 7,5 g/L, reaksiyon süresi 60 dk ve başlangıç Pb(II) konsantrasyonu 50 mg/L olarak belirlenmiştir. Bu deneysel koşullar altında, maksimum Pb(II) giderimi %97 olarak elde edilmiştir. Çalışmanın sonuçlarına göre, balık pullarından elde edilen hidroksiapatit, birçok adsorban materyale kıyasla yüksek verimlilik değerlerine ulaşmak için adsorpsiyon yöntemi ile sudan Pb(II) iyonlarını uzaklaştırmada oldukça verimli bir materyal olarak bulunmuştur.

Anahtar Kelimeler: Balık pulu, deniz levreği, hidroksiapatit, kurşun, adsorpsiyon, atıksu, giderim

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INTRODUCTION

Wastewater must undergo appropriate treatment methods to reach a level that does not threaten the environment and human health before discharged to the receiving environment. Industrial wastewaters especially contain many harmful compounds particularly depending on the type of industry from which they originate. Lead (Pb) is a heavy metal with high toxic effect potential and dangerous in terms of environment and human health. Lead ions are present commonly in many industrial wastewaters, so they are considered as one of the important contaminant worldwide. For this reason, when environmental protection legislation and public environmental issues are taken into consideration, to search for new techniques to separate from industrial wastewater is encouraged.

Sorption is the process of attaching a substance in a solution to the surface or inside of another solid substance. The adsorption method is one of the separation techniques that allows the pollutant removal from water and recycling (by desorption) (Pai et al., 2020). Many studies have been carried out to remove Pb(II) from water, and many adsorbents have been used as raw materials or as modified surfaces. The common feature of these studies is to find adsorbents that are relatively efficient, low cost and easily available for the adsorption of lead ions from wastewater. Hydroxyapatite (HAp) is a natural mineral presented in the structure of hard tissues of vertebrates such as teeth, bones and scales (Trakoolwannachai et al., 2019), and the main feature is hard and strong structure. The mineral component of hydroxyapatite is mainly composed of calcium and phosphate, and its chemical formula is $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Although HAp has been widely used in the regeneration of bones in dental and orthopedic applications, it is now being used in wastewater treatment to remove different pollutants in water. Therefore, HAp which is obtained from natural sources or can be synthesized by different methods, appears as a promising material in water pollution control studies due to its high pollutant holding and ion exchange capacity and thermal durability (Ibrahim et al., 2020). It is possible to use HAp in powder or granule form, and different methods such as sol-gel (Phatai 2019), hydrothermal (Chen et al., 2020), ultrasound-microwave (U-M) (Nyoo et al., 2014), co-precipitation (Banerjee et al., 2018) and sono-chemical (Utara & Klinkaewnarong, 2015) for HAp synthesis have been tried in the literature.

If hydroxyapatite is to be used to remove contaminants such as heavy minerals from water, it is of great importance to determine the mechanism by which sorption process takes place. Because this mechanism shows the behavior of the pollutant in aqueous solution. The main idea of the present study to evaluate wastes arise from fish markets. With this aim, fish scales were used, and the most consumed fish species were evaluated in the evaluation of scales. Therefore, we used fish scales of European seabass (*Dicentrarchus labrax*) to prepare HAp as adsorbent material. It is thought that this study will lead other researchers in the use of fish scale wastes as a source for hydroxyapatite synthesis in waste management in accordance with the principles of zero waste within the scope of sustainable environment. Thus, FS-HAp particles were synthesized in this study, and then it was assessed as adsorbent material to remove Pb(II) ions from aqueous solution.

MATERIAL AND METHODS

Chemicals

All chemicals used in this research were analytical grade (Merck). Stock solution of Pb(II) was prepared from the $\text{Pb}(\text{NO}_3)_2$.

Preparation of the Hydroxyapatite (FS-HAp) from NaOH-treated Fish Scales of Seabass

The raw fish scales (FS) of European Seabass (*Dicentrarchus labrax*) were collected from sellers in the fish markets in Kahramanmaraş. The FS was washed repeatedly with deionized water to remove soluble impurities from their surface, and left to air dry in the laboratory. Then, according to Kongsri et al. (2013), FS was soaked with 0.1 M HCl to remove remaining proteins, heated and stirred at 70 °C for 5 h with 5% NaOH solution. The thermally pretreated FS were treated with a 50% w/v NaOH solution at 100 °C for 1 h to produce inorganic-rich adsorbent. The resulting solution was washed with deionized water to reach neutral pH, and the neutralized adsorbent was dried in the oven. After the dried fish scales were grinded and passed through a 100 µm pore diameter microcellular, powder FS-HAp in the same grain size was obtained (Pon-On et al., 2016).

HAp has low solubility in the pH range of 4.56-9.67 (Kamieniak et al., 2018). At low pH values, the phosphate and hydroxyl ions in the structure of HAp pass into the water and therefore HAp dissolves in a high acidity environment (Ferri et al., 2019). Thus, the high solubility of hydroxyapatite in highly acidic solutions is of great importance in determining the basic characteristics of the solution in which the adsorbent product will be used.

Characterization of the Adsorbent

The morphological characterization and the chemical composition of the FS-HAp particles were investigated by Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis (SEM-EDX). The functional groups of the adsorbent were analyzed by Fourier Transform Infrared Spectrophotometer (FTIR). The pH was determined using a Hanna HI 2211 pH/ORP pH-meter. The Pb(II) concentrations were determined using an ICP-OES (Optima 2100-Perkin Elmer). All the metal adsorption experiments were performed in triplicate.

Experiments

Optimization of pH

Eight solutions with different pH (2.0-9.0) were prepared to investigate the effect of pH on Pb(II) adsorption by HAp. Subsequently, 12.5 g/L FS-HAp was added to each solution having different initial Pb(II) concentrations of 10 and 50 mg/L, and experiment duration was adjusted to 150 min. Since lead ions were expected to precipitate as hydroxides at pH > 9.0, the maximum pH value was chosen as pH 9.0.

Optimization of FS-HAp Amount

The amount of FS-HAp was optimized at the optimum pH. Different amounts of FS-HAp (2.5-22.5 g/L) were added to 50 mL solutions containing 10-50 mg/L Pb(II), and experiments were conducted for 150 min.

Optimization of Time and Concentration

Experiments were carried out at constant pH (optimum), adsorbent concentration (optimum), and different Pb(II) initial concentrations of 5.0-200 mg/L for 15-360 min to find optimal conditions.

Kinetic study

Adsorption kinetics express how the process changes depending on time and the behavior of the adsorbent in solution. For the kinetic studies, 7.5 g/L of FS-HAp was added into 50 mL flasks at pH 4.0 and containing 50 mg/L Pb(II). The change of Pb(II) concentration in the solution was measured by sampling at different times by continuously mixing the mixture for 60 minutes. The purpose of this process is to determine the time when the Pb(II) concentration in the solution reaches equilibrium. Zero-order (Eq. 1), first-order (Eq. 2), and second-order (Eq. 3) kinetic models were used to describe the removal kinetics of Pb(II) by FS-HAps.

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (1)$$

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

$$q_e = k_p t^{0.5} \quad (3)$$

where; q_e and q_t show the amounts of adsorbate on the adsorbent at equilibrium and at any time of t (mg/g). k_1 is the rate constant of first-order sorption (1/min), k_2 (g/mg.min) is the rate constant of second-order adsorption, and k_p is the rate constant for pore diffusion model (mg/g 1/2); $t^{0.5}$ is half time (min).

Adsorption Isotherms

The adsorption equilibrium data were analyzed using the Langmuir (Eq. 4), Freundlich (Eq. 5) and Dubinin Radushkevich (D-R) (Eq. 6, 7) adsorption isotherm models:

$$\frac{1}{q_e} = \frac{1}{b q_m C_e} + \frac{1}{q_m} \quad (4)$$

$$\ln q_e = \ln K_f + \frac{1}{n \ln C_e} \quad (5)$$

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (6)$$

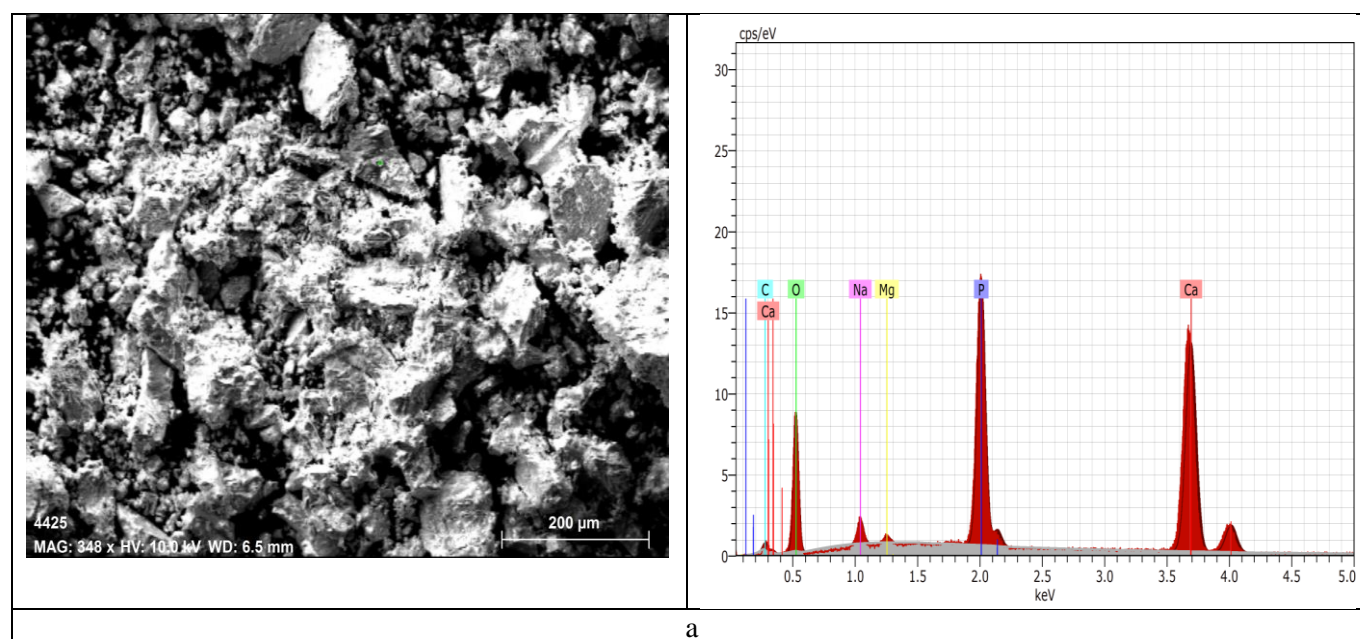
$$\ln q_e = \ln X_m - K \varepsilon^2 \quad (7)$$

where; C_e is Pb(II) concentration in equilibrium (mg/L), q_m is maximum capacity of FS-HAp for Pb(II) adsorption (mg/g), K_f and b are the coefficients of Freundlich and Langmuir models, and n is the exponent of Freundlich model. X_m is maximum capacity of FS-HAp for Pb(II) adsorption (mg/g), K is isotherm constant, ϵ is Polanyi adsorption potential (kJ/mol), R is gas constant (8.314 J) and T is temperature ($^{\circ}\text{K}$)

RESULTS AND DISCUSSION

Adsorbent Characterization

EDX results for the raw FS-HAp obtained from FS, and treated FS-HAp after the adsorption treatment were presented in Fig. 1. In the EDX analysis carried out at one point of the adsorbent, and the presence of elements in the structure of the adsorbent appear before the adsorption. The main structure of raw FS-HAp composed of calcium (52.85 % wt.), oxygen (25.01% wt.) and phosphorus (19.32 % wt.). The results of EDX analysis indicate that lead ions are attached to adsorbent after adsorption and in this case the adsorption process is performed successfully. After the adsorption process, its EDX analysis showed that it contains 30.42% Ca, 13.35% O, 11.37% P, and 44.16% Pb(II) in its mass. After the adsorption process, the percentages of calcium and phosphorus in the content decreased and lead (44.16 % wt.) was added to this mass structure of FS-HAp. It implies that Pb(II) has been adsorbed on the surface of FS-HAp successfully. In addition, the decrease in the calcium and phosphorus content in the FS-HAP content after the adsorption process can be explained by the replacement of these anions by Pb (II) ions. As seen from the analysis of SEM, it is seen that each particle structure is different. The physical and chemical structure of the adsorbent is an important factor affecting the rate and efficiency of the adsorption. The size of the surface area of the adsorbent and the small size of the particle structure are also the factors affecting the adsorption efficiency. Increasing surface area and decreasing particle size positively affect adsorption.



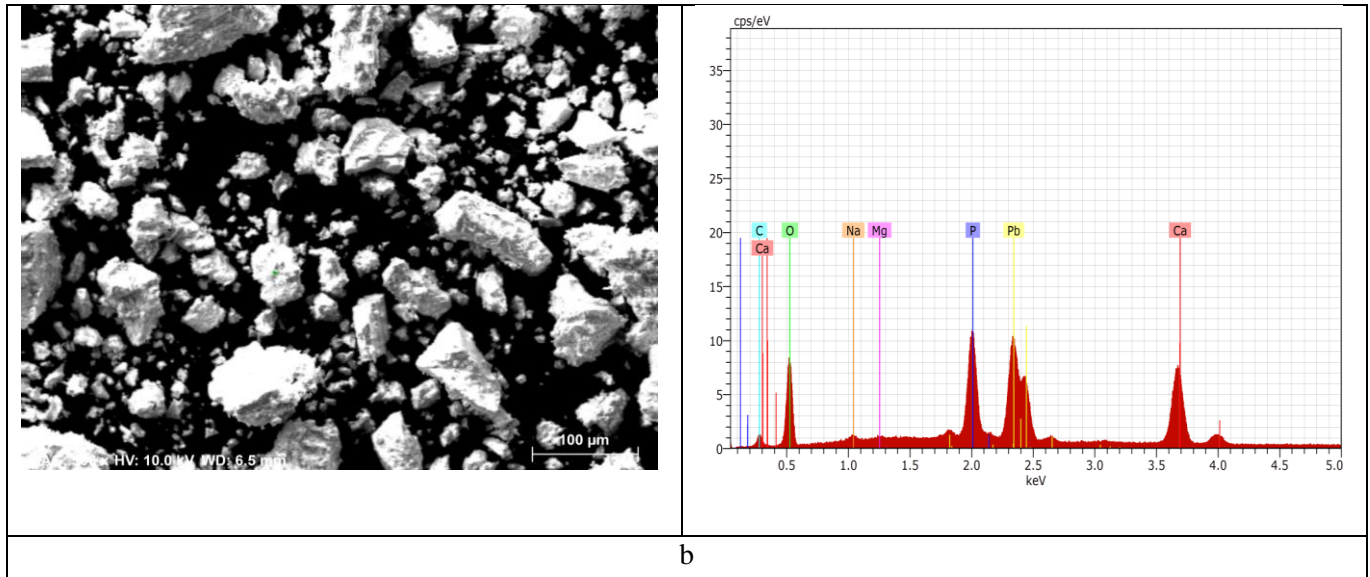


Figure 1. Elemental Analysis of FS-Hap Before (a) and After the Adsorption (b).

FTIR analyses were also performed to identify the adsorbents before and after the adsorption process, and spectra were obtained as below (Fig. 2). In the FTIR spectrum, the signaling of the oxygen-hydrogen (OH) bonds was observed in the strong broad peak at 3361 cm^{-1} regions. The medium strength peak of 1644 cm^{-1} corresponds the C=C stretching. The peaks of $416\text{--}600$ are considered to belong to the low phosphate bonds, and the peaks in the area of $1416\text{--}1410\text{ cm}^{-1}$ and $962\text{--}1017\text{ cm}^{-1}$ considered to belong to the high phosphate bonds (Chen & Chang, 2012). The weak peaks in the $871\text{--}875\text{ cm}^{-1}$ regions are considered to the carbonate bands. When the FTIR spectra after adsorption were examined, it was interpreted that peaks at 3361 cm^{-1} and 1644 cm^{-1} regions were relatively lost after the adsorption, and lead could be bounded to the bonds in these regions.

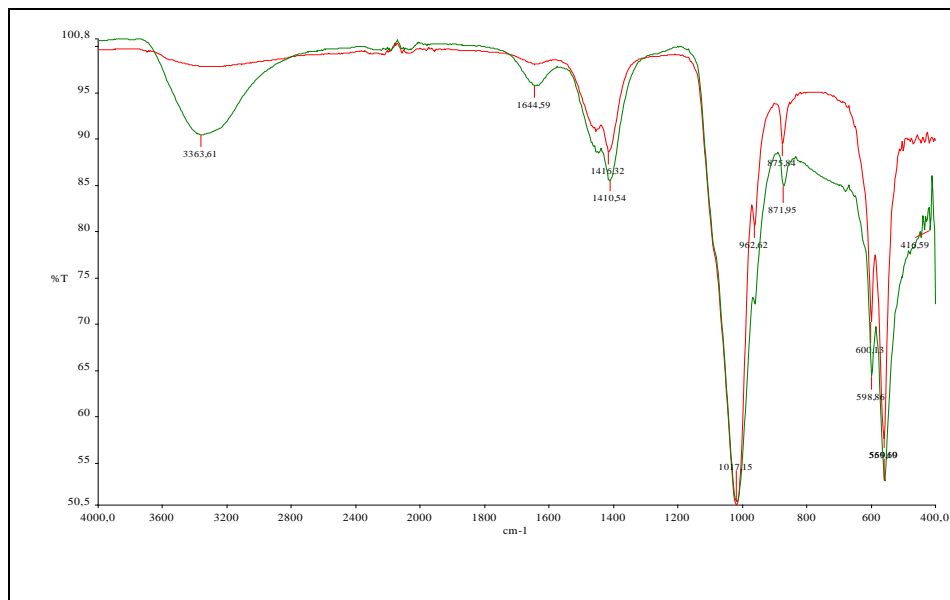


Figure 2. FTIR Analyzes Before (Green Line) And After (Red Line) The Adsorption Process of The FS-Hap

SEM surface analyses of the adsorbent before and after the adsorption were occurred, and the following images were obtained (Fig. 3). It was seen that the hydroxyapatites had a smooth and porous surface structure before the adsorption process. The comparison of Fig. 3 (a, b, c) with (d, e, f) reveals that the particles adhered together, pores and cavities closed, and formed a more compact structure after the adsorption.

a

b

c

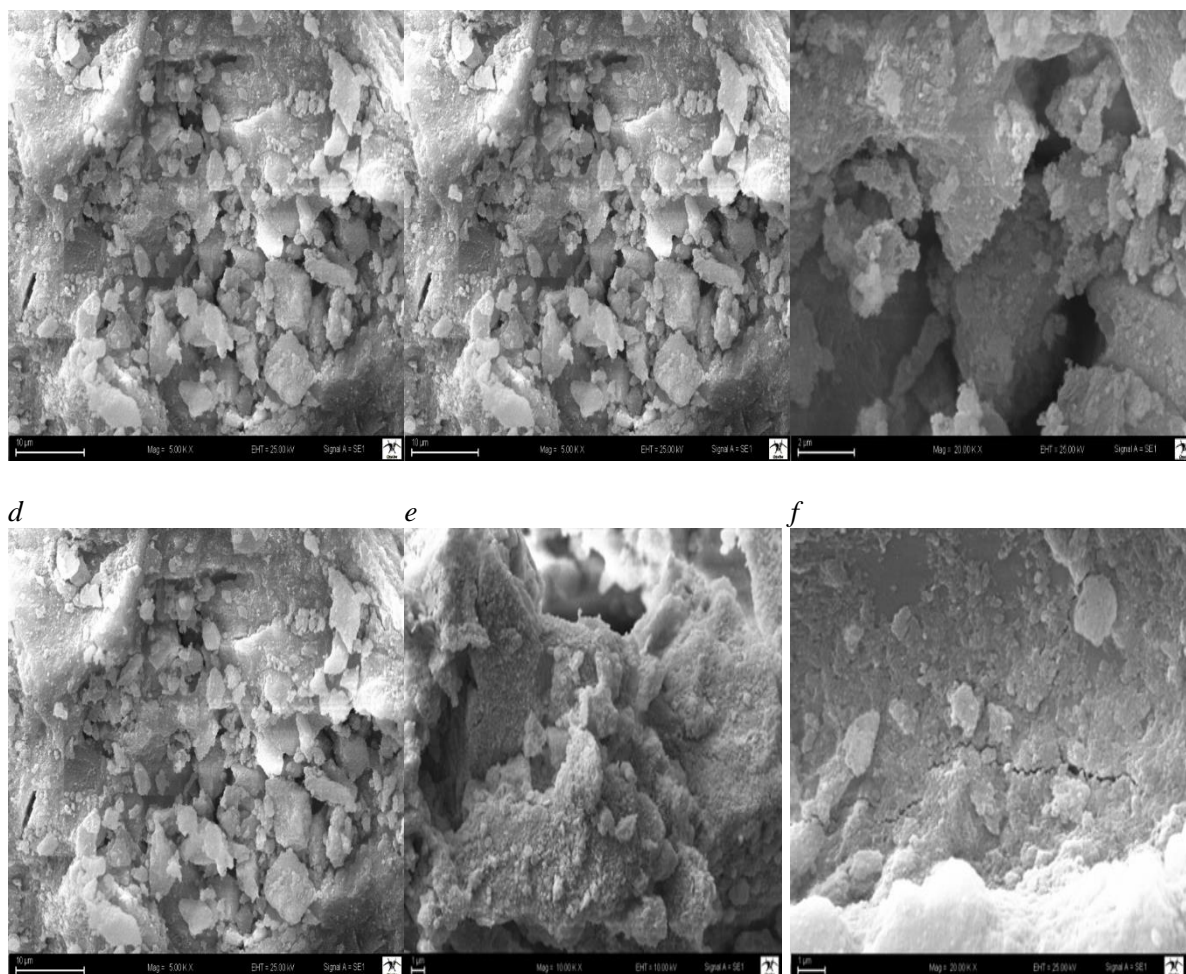


Figure 3. SEM Surface Analyses of FS-Hap Particles Before (a: Mag 5.00 KX, b: 10.00 KX, c: 20.00 KX) and After (d: 5.00 KX, e: 10.00 KX, f: 20.00 KX) the Adsorption Process

Batch Adsorption Experiments

The Change of Pb(II) Adsorption by FS-Hap with pH

pH is one of the most fundamental parameters having the effect on the efficiency of any water treatment application. Because the pH of the aquatic environment directly affects the solubility of the substances it contains and the surface charge of the adsorbent when it is said on the basis of the adsorption process. In order to investigate the effect of different initial pH on adsorption process, the pH effect on adsorption process was studied by adding FS-HAP nanoparticles (12.5 g/L) to the flasks containing 10 and 50 mg/L Pb(II) ions at different pH (2.0-9.0) for 150 min. at room temperature (Figure 4).

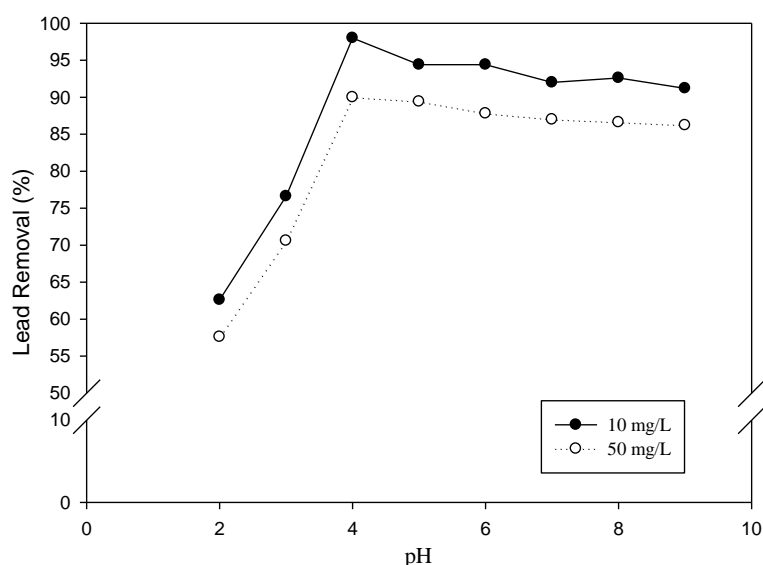


Figure 4. pH Effect on Lead Removal by FS-HAp
(pH: 2.0-9.0, C_0 : 10-50 mg/L, FS-HAp: 12.5 g/L, t: 150 min)

It is clearly seen from Figure 4 that the adsorption of Pb(II) on to FS-HAp increased with increasing pH up to pH 4.0, then adsorption efficiency of the adsorbent decreased with increasing of solution pH. This positive effect on adsorption revealed the pH had strong effect on the process. According to the experimental results, the best removal efficiencies were obtained at pH 4.0 as 98% and 90% for 10 mgPb(II)/L and 50 mgPb(II)/L, respectively. The reason of this; the predominant types of metals below pH 5.0 is divalent, and all of the metal ions are completely soluble in the solution and therefore no precipitation (Haşimi, 2006). At low pHs (pH<3.0), Pb(II) ions are competing with H^+ ions that want to settle in active adsorption sites. This reduces metal ion adsorption. At high pHs (pH> 5.5), lead is precipitated as $Pb(OH)_2$ (Gupta et al., 2012). The predominant removal mechanism at pH 2.0 and 3.0 was the dissolution of FS-HAp followed by precipitation of hydroxypyromorphite. It was also stated that Ca(II) and Pb(II) in FS-HAp structure were replaced by cation exchange reaction at pH 4.0 and 5.0. Thus, in the present study, optimum pH for Pb(II) adsorption was fixed at 4.0 for the next steps of the adsorption experiments. Thanh et al. (2018) used the magnetite-hydroxyapatite nanocomposite for the removal of Cu (II) and Ni (II) ions from the solutions. In order to determine pH effect on the adsorption process, they tried different pH ranges of (3.0-5.0) and (3.0-7.0), and they found optimum pH values for Cu (II) and Ni (II) adsorption as 5.0 and 7.0, respectively.

The Change of Pb(II) Adsorption by FS-Hap with Its Concentration

Adsorbate concentration in the solution changes the adsorption capacity and reaction rate. Since the amount of adsorbent per unit volume will vary at different concentrations, the amount of adsorbate adsorbed by the adsorbent will also change. Experiments were carried out at room temperature (22 ± 1 °C) for 150 min using the amount of adsorbents in the range of 2.5-22.5 g/L at pH 4.0 in order to find optimum adsorbent concentration for Pb(II) removal by FS-HAp (Fig. 5). As seen in Fig. 6, Pb(II) removal efficiency for both concentrations of 10 and 50 mg/L increased by increasing of adsorbent concentration linearly. The surface area and number of active sites increased with increasing of adsorbent concentration which leads to high Pb(II) removal. The maximum removal efficiency was obtained at the maximum adsorbent concentration of 22.5 g/L as 98.2% and 93.2 for both of the Pb(II) concentrations of 10 and 50 mg/L while, these values were found as 89% and 92% for 2.5 g/L adsorbent concentration, respectively. The removal efficiency of the adsorbent at lowest adsorbent concentration of 2.5 g/L is very close to the removal efficiency obtained when working with the highest adsorbent concentration of 22.5 g/L, this result demonstrates how successful the hydroxyapatite obtained from fish scale wastes is in the removal of lead ions. For this reason, optimum FS-HAp dose was chosen as 7.5 g/L (with 95 and 90% removal efficiencies) for next set of the experiments. It has been stated that with increasing adsorbent concentration, suitable surface areas and adsorption zones for Pb(II) ions increase, and thus removal efficiency increases.

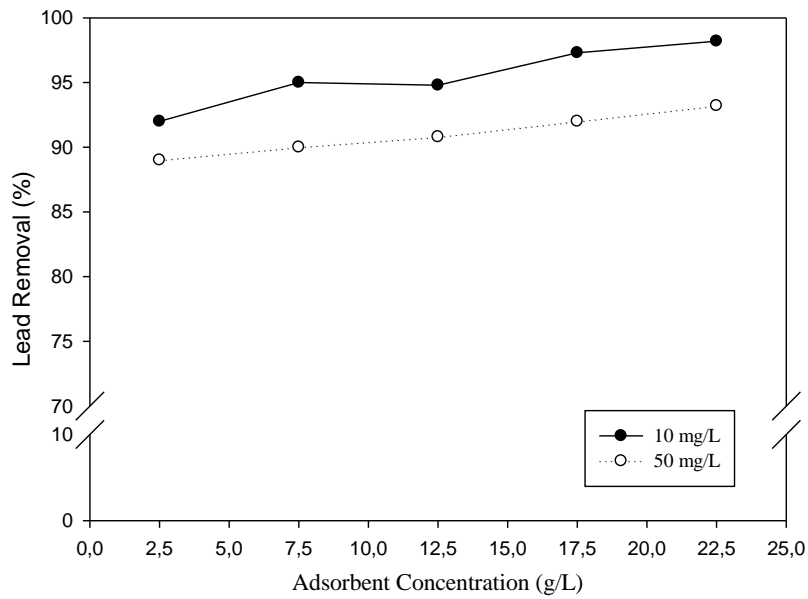


Figure 5. Adsorbent Concentration Effect on Lead Removal by FS-HAp (pH:4.0, C₀: 10-50 mg/L, FS-HAp: 2.5-22.5 g/L, t:150 min)

The Change of Zn(II) Adsorption by Concentration and Time

Since industrial wastewater contains heavy metal ions in different concentrations and types depending on the type of industry, it is an important factor to know the amount of heavy metals present in the raw wastewater in adsorption studies. Thus, determination of its effect is so important for adsorption process. The effect of Pb(II) amount on the adsorption by FS-HAp was studied by varying the initial Pb(II) concentrations of 5 to 200mg/L in the test solution, keeping all other parameters constant (pH: 4.0, FS-HAp: 7.5 g/L, t: 360 min, T: 22±2°C). The amount of Pb(II) adsorbed decreased with increasing initial Pb(II) ion concentration because of the solution’s adsorbent concentration was constant and it tends to saturation at higher Pb(II) concentrations (Fig. 6). The maximum removal efficiency was obtained as 93% for 5 mg Pb(II)/L while, it decreased to 84.6% in 200 mg Pb(II)/L. It can be seen that this value is quite high for such a high lead concentration for 200 mg/L. It was decided to choose optimum initial concentration of Pb(II) as 50 mg/L because of high removal efficiency of 90% was achieved.

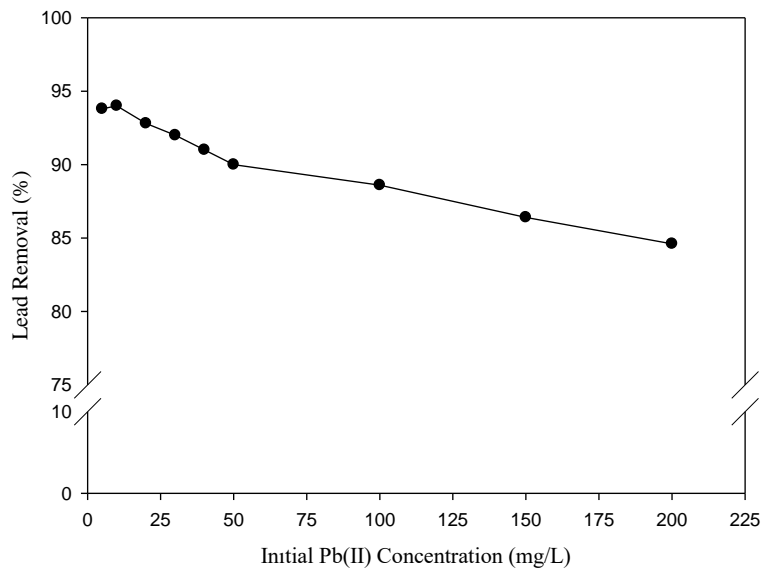


Figure 6. The Change of Pb(II) Removal by Initial Pb(II) Concentration (pH:4.0, C₀: 5-200 mg/L, FS-HAp: 7.5 g/L, t:60 min)

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 determine the effect of contact time on the adsorption, experiments were conducted keeping all other parameters constant (pH: 4.0, adsorbent concentration: 7.5 g/L, and 10-150 mgPb(II)/L) for 15-360 min. According to Fig. 7, the removal efficiencies for each studied Pb(II) concentrations reached the maximum in the first 60 minutes (97-80% range), and they decreased slightly when the reaction time was extended to 360 min. However, this decrease was not significant because of the removal efficiencies were still in the range of 92-72.3% range. As predicted, removal efficiencies decreased with increasing of Pb(II) concentrations.

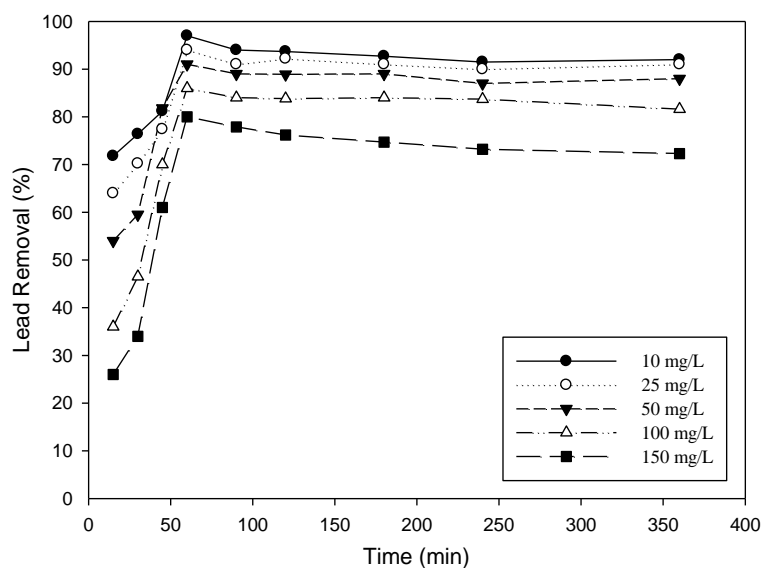


Figure 7. The Change of Pb(II) Removal By Reaction Time (pH: 4.0, C_0 : 10-150 mg/L, FS-HAp: 7.5 g/L)

Adsorption Kinetics

Kinetic experiments are made to understand the adsorption mechanisms such as chemical and/or physical reaction and diffusion. With this aim, time-adsorption capacity results were fitted to the first-order, second-order, and intra-particle diffusion models, and adsorbent/adsorbate relationships were determined between Pb(II) and FAS-HAp. Figure 8 shows the linear plots of Lagergren first-order, Lagergren second-order and intra-particle diffusion models for the sorption of Pb(II). The correlation coefficients (R^2) for each model were checked and parameters of each model were summarized to see which of the examined models explain the kinetic results of our study better (Table 1).

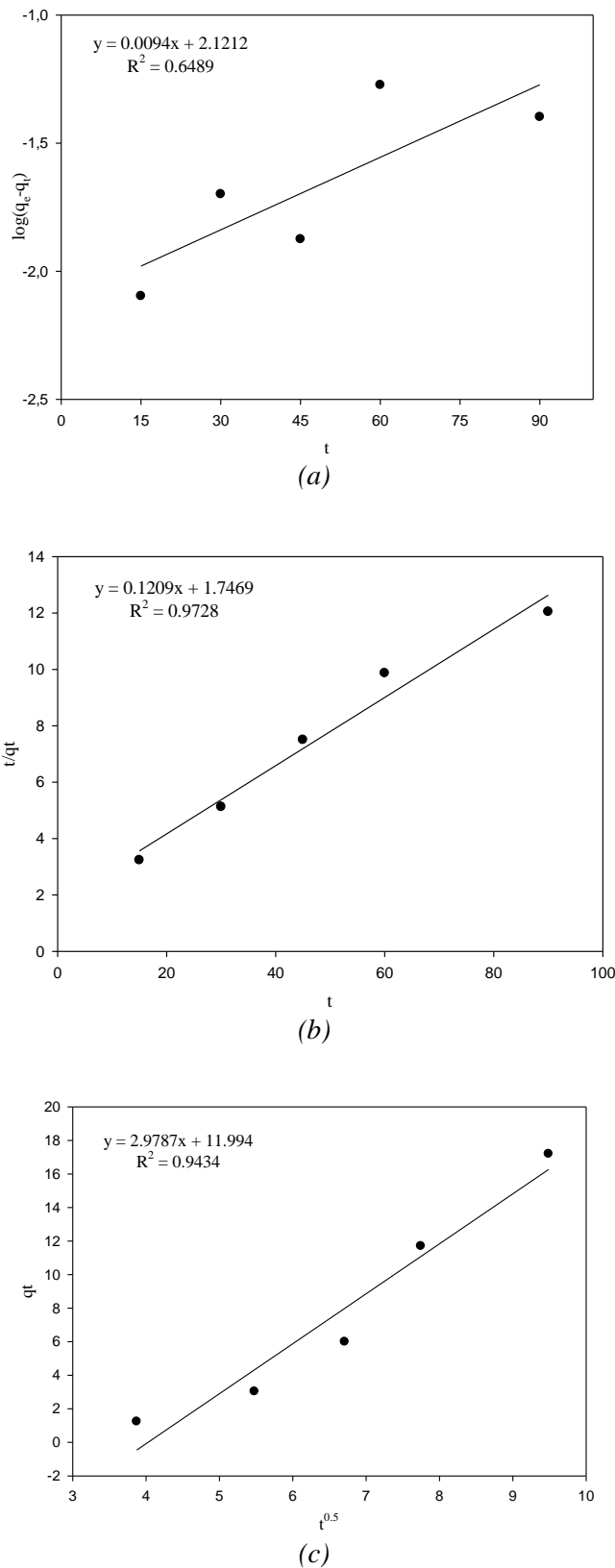


Figure 8. The Pseudo First Order (a): Pseudo-Second Order (b): And Intraparticle Diffusion (c): Models for Pb(II) Removal by FS-Hap

The pseudo second order equation with R^2 values of 0.973 for FS-Hap was found to be best kinetic equation describing Pb(II) adsorption kinetic on hydroxyapatite powders followed by the diffusion-controlled process which is the intraparticle (pore) diffusion model (R^2 : 0.943). The results showed that not only the surface adhesion or

surface chemistry is effective on the adsorption rate but also closely related to the pore structure of the hydroxyapatite at the micro or macro grade. The results also showed that in the adsorption process, firstly, Pb (II) ions were rapidly transported to the surface of the adsorbents and then diffused into the particles (Harja & Ciobanu, 2018).

Table 1. Kinetic Parameters for Pb(II) Adsorption onto FS-HAp (pH: 4.0, FS-HAp: 7.5 g/L, 50 mg Pb(II)/L, T: 22±2 °C)

Kinetic models	Parameters	Value
Pseudo-first order kinetic	q_e (mg/g)	18.74
	k_1 (min ⁻¹)	0.02
	R ²	0.649
	SS	3330
	MS	832.5
	P	0.1
Pseudo-second order kinetic	q_e (mg/g)	133.333
	k_1 (g/mg.min)	0.007
	R ²	0.973
	SS	3330
	MS	832.5
	P	0.002
Intraparticle diffusion	q_e (mg/g)	11.994
	k_p (mg/g.min ^{0.5})	2.9787
	R ²	0.943
	SS	18.339
	MS	4.585
	P	0.006

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

Adsorption Isotherms

In the adsorption processes, removal of a material from the solution continue until an equilibrium to be form between the adsorbent and adsorbate. Results of the isotherm studies are applied on the selection and to determine the potential efficiency of the adsorbent to be used before the results are put into practice in real scale. Process feasibility can be assessed for a given application by using experimental isotherms for example the most suitable adsorbent or the adsorbent dosage requirements can be determined. The regression coefficients of the three 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 Pb(II) Adsorption On FS-HAp

Isotherms	Parameters			
Langmuir	R ²	b	q_m	R_L
	0.9588	0.040	39.52	0.33
Freundlich	R ²	K_f	n	
	0.9989	1.91	1.370	
Dubinin Radushkevich	R ²	K	X_m	ϵ
	0.9256	2x10 ⁸	3.66	5.0

The correlation coefficients (R²) for Freundlich and Langmuir models were found to be higher than the correlation coefficients of the D-R isotherm model for FS-HAp. Freundlich model explained the isotherm behavior of adsorbents very well. According to the R² values, the Freundlich model defined the adsorption of Pb(II) on the FS-HAp very well and revealed that the adsorption on the surface occurs in the form of multiple layering. Particularly, the 1/n value (0.730), which is close to 1, proves that the binding regions are homogeneously distributed on the adsorbent surface. In addition, the separation factor (R_L) of Langmuir model was found to be between 0 and 1 (0.33), this indicated a favorable sorption process. The maximum Pb(II) adsorption capacities obtained by unit adsorbent mass were calculated from Langmuir model as 39.5 mg/g. The Langmuir model shows that binding sites of adsorbent have an equal affinity for the adsorbate, and adsorption occurred with the formation of a monolayer. In the D-R isotherm, the ϵ takes a value between 8-16 kJ/mol according to what is expressed in the Polanyi potential,

and if it is below 8 kJ/mol, the adsorption process is expressed physically and if greater than 8 kJ/mol, the adsorption process is expressed chemically. According to this study, it can be said that the adsorption process is physical. The values of the mean sorption energy (ϵ) of 5 kJ showed that there was a chemical bonding and chemisorption (chemical adsorption).

CONCLUSIONS

In this study, an environmentally friendly adsorbent was synthesized from waste fish scales (FS-HAP) to investigate the removal potential of Pb(II) ions from solutions by adsorption method. The results of this study represented the usability of waste fish scales as a valuable, renewable and low-cost adsorbent material in terms of waste minimization. Adsorption experiments were made to show the change of the adsorbent behavior in different aqueous media with different pH and Pb(II) concentrations, and the results obtained showed that the adsorption reactions took place quickly and reached the maximum removal value with 7.5 g/L FS-HAP in the first 60 minutes. In these conditions, FS-HAP exhibited quite high Pb(II) removal ability (97%). Hydroxyapatite synthesized from fish scales has been found to be a reliable adsorbent material for lead removal from wastewater in treatment applications.

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