Effect of the Experimental Conditions on the Adsorption Capacities in the Removal of Pb^{2+} from Aqueous Solutions by the Hydroxyapatite Nanopowders

Oral Lacin, Turan Calban, Fatih Sevim, Taner Celik

Abstract—In this study, Pb^{2+} uptake by the hydroxyapatite nanopowders (n-Hap) from aqueous solutions was investigated by using batch adsorption techniques. The adsorption equilibrium studies were carried out as a function of contact time, adsorbent dosage, pH, temperature, and initial Pb^{2+} concentration. The results showed that the equilibrium time of adsorption was achieved within 60 min, and the effective pH was selected to be 5 (natural pH). The maximum adsorption capacity of Pb^{2+} on n-Hap was found as 565 mg.g^{-1}. It is believed that the results obtained for adsorption may provide a background for the detailed mechanism investigations and the pilot and industrial scale applications.

Keywords—Nanopowders, hydroxyapatite, heavy metals, adsorption.

I. INTRODUCTION

THE presence of heavy metals in the aquatic system is harmful to humans, plants, and animals [1]. One of the most commonly-used heavy metals is lead and lead compounds. Lead (Pb) is a very toxic heavy metal, found in the earth's crust with an average concentration of 16 mg/kg in soils. World Health Organization (WHO), United States Environmental Protection Agency (USEPA), and European Union (EU) have set permissible limit of Pb^{2+} in drinking water to be 0.010, 0.015, and 0.010 mg/L, respectively. Additionally, according to the WHO more than 3.5 million people die every year due to the heavy metal's presence in water [2], [3]. On the other hand, lead has been extensively used in various industries such battery manufacturing, ceramic and glass manufacturing, metal planting and finishing, printing, bullets, and production of lead additives for gasoline [4], [5]. In this context, many researchers have focused their attention to develop different methods for the lead removal from wastewaters. Among the methods which have been already used, chemical precipitation, adsorption, ion-exchange, membrane separation, reverse osmosis, and electrochemical reduction could be mentioned. Compared with the other treatment methods, adsorption appears to be an attractive process because it is simple, effective, and economical [6]. Furthermore, previous studies have revealed that apatite minerals are able to successfully remove lead from the aqueous solutions [7]. The best known member of the apatite family is hydroxyapatite. The previous studies have shown that Pb^{2+} ions exchange rapidly with Ca, and this process induces morphological changes in the surface region [8]-[10]. Recently, using the synthetic nano hydroxyapatite as adsorbents has become a hot topic in chemistry. Hydroxyapatite has six square crystal systems which contribute to its strong ability of ion exchange. As a kind of strong ion exchanger, metal ions on the surface of hydroxyapatite could exchange heavy metals such as Pb^{2+}, Hg^+, Cr^{6+}, Cd^{2+}, Ni^{3+}, and so on [11]-[14]. For this purpose, the use of n-Hap in removing Pb^{2+} from the aqueous solutions has been studied as a function of various adsorption conditions, such as contact time, adsorbent dosage, pH, temperature, and initial Pb^{2+} concentration.

II. MATERIALS AND METHODS

All the chemicals used in the experiments are analytical grade. The standard stock solution of 10.000 mg.L^{-1} Pb^{2+} was prepared by dissolving 31.968 g $Pb(NO_3)_2$ in 2 L of deionized water. The other lower concentrations were obtained by diluting the stock solution freshly for each experiment. The n-Hap was synthesized by sol-gel method and was submitted by [15].

Adsorption studies were conducted by using an air bath mechanical shaker (Edmund Buhler Gmbh TH15). The experimental process was given in Fig. 1.

Adsorption measurements were carried out in a well-mixed glass flask (150 ml) heated at a desired-temperature and equipped with an air bath mechanical shaker. After 50 ml of desired concentrations of Pb^{2+} solutions were added to the glass flask and the temperature was set at the desired value, predetermined amounts of n-Hap were added to the glass flask. This content was stirred at a certain speed and pH. Each experiment was carried out according to the parameters shown in Table I.

The solid phase was separated from the mixture by centrifuging after adsorption. 10 ml samples from liquid phase were taken, and then analysed for the contents of Pb^{2+} by

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using a Shimadzu AA-670 atomic absorption spectrometer (AAS). All measurements were made after the optimisation of the following parameters: wavelengths 283.3 nm for Pb, flame air / C_2H_2, and detection limit 0.05 ppm.

Adsorption capacity of the Pb^{2+} was determined as follows (q_e, mg.g^{-1}):

$$q_e = (C_o - C_t)\frac{v}{m}$$

where C_0 & C_t (mg.L^{-1}) = The initial and residual concentration of the Pb^{2+}, v (L) is the volume of aqueous solution containing Pb^{2+}, and m (g) is the mass of n-Hap adsorbent.

Contact time, adsorbent dosage, pH, temperature, and initial Pb^{2+} concentration on the Pb^{2+} adsorption were studied. Each experiment was repeated twice and given results were the average values.
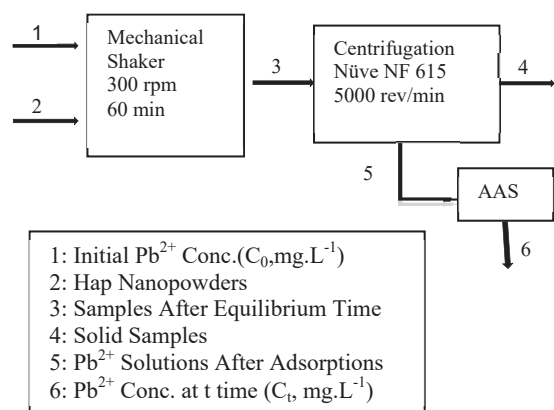

Fig. 1 The Experimental Process

TABLE I
PARAMETERS AND THEIRS VALUES SELECTED

Contact time (min)	1	2	5	10	20	40	60	90
Adsorbent dosage (g.L^{-1})	1	2	3	4				
Initial Pb^{2+} Concentration (mg.L^{-1})	500	1000	1500	2000	2500			
Temperature (°C)	25	30	35	40				
pH	2	4	6	8				

III. RESULTS AND DISCUSSION

A Effect of Contact Time on Pb^{2+} Adsorption

Determining the equilibrium time is one of the most important parameters of adsorption studies. Hence, the effect of contact time was studied at an initial Pb^{2+} concentration of 1500 mg.L^{-1} (50 mL solution), adsorbent dose of 2 g.L^{-1}, temperature 25 °C, stirring speed 200 rpm, and natural of pH of 5. The contact time was varied from 1 min to 90 min. The experimental results were shown in Fig. 2. It can be noticed from Fig. 2 that the Pb^{2+} adsorption percent was fast at the initial stages and gradually became slower until the equilibrium is attained. The optimal contact time to attain the equilibrium was experimentally found to be about 60 min. For the subsequent experiments, it was carried out as 60 min.
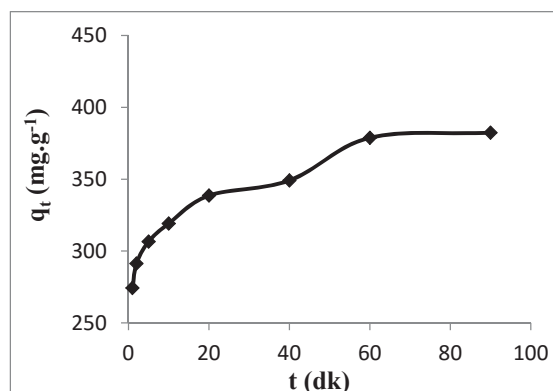

Fig. 2 Effect of contact time on Pb^{2+} adsorption at adsorbent dosage=2g.L^{-1}, C_0=1500 mg.L^{-1}, natural pH=5, T=25 °C, and stirring speed 200 rpm

B. Effect of Adsorbent Dosage on Pb^{2+} Adsorption

The experimental results of the adsorption of the Pb^{2+} on n-Hap as a function of adsorbent dosage (1 - 4 g.L^{-1}) at contact time of 60 min, an initial Pb^{2+} concentration of 1500 mg.L^{-1} (50 mL solutions), natural of pH of 5, temperature 25 °C, and stirring speed 200 rpm are shown in Fig. 3. As can be seen in Fig. 3, the Pb^{2+} adsorption percent rapidly increased with the increase in the adsorbent dosage from 1 g.L^{-1} to 3 g.L^{-1}. This can be attributed to higher adsorbent dosage due to the increased surface area providing more adsorption sites available which gave rise to higher removal of Pb^{2+}. Then, there is a slight decline with an increase in the adsorbent dosage from 3 g.L^{-1} to 4 g.L^{-1}. This trend can be attributed to the formation of clusters of exchanger particles resulting in decreased effective surface area [16].

C. Effect of pH on Pb^{2+}Adsorption

The amount of Pb^{2+} adsorbed varies with the pH of aqueous medium. The experimental results of the adsorption of the Pb^{2+}on n-Hap as a function of pH (2-10) at contact time of 60 min, an initial Pb^{2+} concentration of 1500 mg.L^{-1} (50 mL solutions), adsorbent dosage of 2 g.L^{-1} and temperature of 25 °C are shown in Fig. 4. As it can be seen in Fig. 4, this adsorption was strongly pH-dependent. The Pb^{2+} adsorption percent increases with the increase in pH from 2 to 8. Significant change in the Pb^{2+} adsorption percent was observed between pH 4 and 6. So, subsequent experiments were carried out for the initial pH of 5.

The low content of protons had little effect on adsorption, resulting in high affinity with Pb^{2+}. When the pH was in the range of 4– 6, most of the active sites were occupied.

The pH of the solution affects the adsorptive process through protonation and deprotonation of functional groups of the active sites of the adsorbent surface. As the concentration of H^+ decrease with the increase in pH, adsorption amount of Pb^{2+} on n-Hap increase [17].
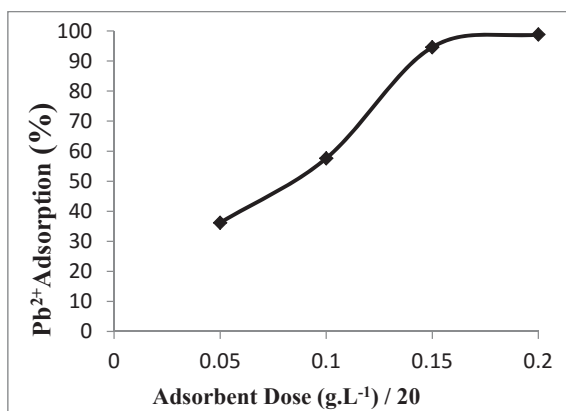
World Academy of Science, Engineering and Technology
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Vol:10, No:8, 2016

Fig. 3 Effect of n-Hap dosage on Pb^{2+} adsorption at contact time 60 min, C_0=1500 mg.L^{-1}, natural pH=5, T=25 °C, and stirring speed 200 rpm
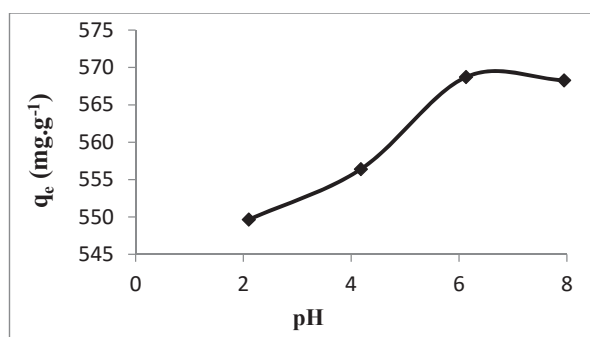

Fig. 4 Effect of pH on Pb^{2+} adsorption at contact time 60 min, C_0=1500 mg.L^{-1}, adsorbent dosage=2g.L^{-1}, T=25 °C, and stirring speed 200 rpm

D. Effect of Temperature on Pb^{2+} Adsorption

The adsorption experiments were performed in the temperature range of 25-40 °C. The experimental conditions were initial Pb^{2+} concentration (500-2500 mg.L^{-1}), natural pH of 5, adsorbent dosage of 2 g.L^{-1}, and contact time of 60 min. The experimental results are shown Fig. 5, and it is revealed that the removal of Pb^{2+} increases with temperature. The removal of Pb^{2+} is favorably adsorbed by n-Hap at higher temperatures, which shows that the adsorption process may be an endothermic reaction [18].
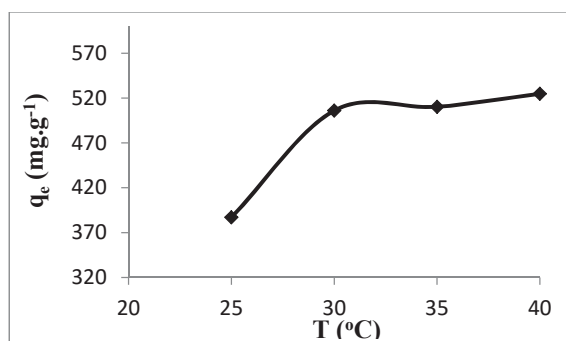

Fig. 5 Effect of temperature on Pb^{2+} adsorption at contact time 60 min, C_0=1500 mg.L^{-1}, adsorbent dosage=2g.L^{-1}, natural pH=5, and stirring speed 200 rpm

E. Effect of Initial Pb^{2+} Concentration

The Pb^{2+} adsorption percent by n-Hap was tested at different initial Pb^{2+} concentrations (500-2500 mg.L^{-1}) and at fixed conditions (temperature 25 °C, natural pH of 5, adsorbent dosage of 2 g.L^{-1}, and contact time of 60 min). The effect of initial ions concentration on Pb^{2+} adsorption percent is presented in Fig. 6. As it can be seen in Fig. 6, the Pb^{2+} adsorption percent decreases with the increase of initial ions concentration of Pb^{2+}. This may be attributed to the sufficient adsorption sites available at lower concentration, which facilitate the Pb^{2+} interaction with the adsorption sites. However, in the case of higher concentration, the adsorption sites of n-Hap are saturated, leading to the decrease in the Pb^{2+} adsorption percent [19], [20].
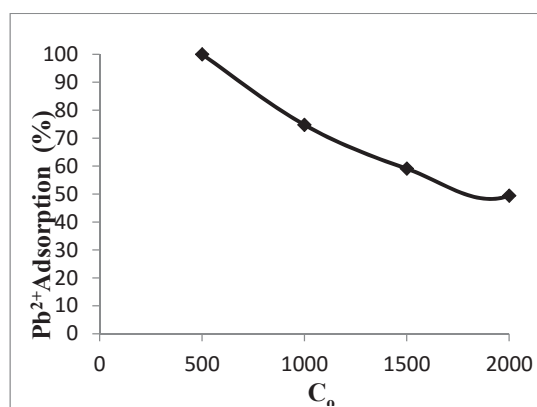

Fig. 6 Effect of initial Pb^{2+} concentrations on Pb^{+2} adsorption at contact time 60 min, T=25 °C, adsorbent dosage=2g.L^{-1}, natural pH=5, and stirring speed 200 rpm

IV. CONCLUSION

The adsorption equilibrium studies were examined as a function of contact time, adsorbent dosage, pH, temperature, and initial Pb^{2+} concentration. The optimal contact time to attain equilibrium was experimentally found to be about 60 min. For the subsequent experiments, it was carried out as 60 min. Pb(II) adsorption on n-Hap was greatly pH-dependent, and increasing pH led to remarkable increase of the adsorption capacity. The maximum adsorption capacity of Pb(II) on n-Hap was found to be about 565 mg.g^{-1} at natural pH 5, temperature of 25 °C, adsorbent dosage of 2 g.L^{-1}, and initial concentrations of Pb^{2+} of 1500 mg.L^{-1}. In the view of these results, it can be concluded that the n-Hap can be utilized as an effective adsorbent for the removal of Pb^{2+} from the aqueous media.

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