Removal of Pb^{2+} from aqueous solutions by rock phosphate (low-grade)

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ABSTRACT

In this study, removal of Pb^{2+} from aqueous solution by adsorption on rock phosphate (low-grade) has been investigated in batch experiments. [1] The Pb^{2+} adsorption capability of the rock phosphate was evaluated as a function of pH, adsorbent dosage, contact time, initial Pb^{2+} concentration and temperature. Adsorption capacity of rock phosphate was found to be 200 mg Pb^{2+}/g of adsorbent for initial Pb^{2+} concentration of 50 mg/L at 25 °C, while the adsorbent dosage was maintained at 0.25 g/L in pH 5 and contact time 120 min. Adsorption data obtained at 25, 35, 45 and 55 °C showed that the adsorption process was well-fitted with the pseudo-first-order adsorption rate expression and Langmuir adsorption isotherm. Activation energy obtained from kinetic data was found to be 33.6 kJ mol^{-1}.

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1. Introduction

Heavy metals such as copper, lead and zinc are main toxic pollutants in industrial wastewater, and they also become major contaminants in surface water and groundwater. The contamination of wastewater and soil with toxic heavy metal ions is a complex problem, which has received much attention in recent years [1]. Among these, lead pollution has been recognized as a potential threat to air, water and soil. Exposure to excessive levels of lead in the environment, at home, and at work place imposes costs, with many millions of adult and children suffering adverse health effects and impaired intellectual development [2]. The conventional technologies for the removal of heavy metal ions from aqueous solution are chemical precipitation, ion exchange, reverse osmosis, electrochemical treatment and sorption [3]. All these procedures present significant disadvantages, such as incomplete removal, high-energy requirements, and production of toxic sludge or waste products requiring disposal. They are also often very expensive. As a result, many alternative methods for heavy metal removal were developed in the last decade [4].

Several natural and synthetic materials have been investigated as adsorbents for heavy metals. Among these, metal oxides and activated carbon are the most extensively employed, but their high costs have limited their large-scale use for the removal of toxic heavy metals [5].

Phosphate minerals have been shown to possess the potential to adsorb heavy metal ions from aqueous solutions [6–13].

High-grade rock phosphate has already found major applications in phosphoric acid and fertilizer manufacturing and hydroxyapatite is too costly to be commercially used. However, the low-grade (<15% P$_2$O$_5$) rock phosphate and pyrophyllite are relatively inexpensive and need to be explored for application in separation of heavy metal ions [14].

Turkey has 300 million tons of low-grade phosphate reserves, which has not been used in phosphoric acid and fertilizer manufacture because of its low P$_2$O$_5$ content (<11% P$_2$O$_5$). The composition of rock phosphate varies from one deposit to another. Therefore, phosphates from different sources are expected to behave differently in adsorption processes.

With this aim, removal of Pb^{2+} from aqueous solutions by using rock phosphate (low-grade) was investigated. The effects of pH, adsorbent dosage, contact time, initial Pb^{2+} concentration and temperature on adsorption capacity were experimentally investigated and the adsorption kinetics has been determined.

2. Materials and methods

2.1. Phosphate treatments and characterization

Rock phosphate (low-grade) used as adsorbent in this investigation was obtained from the phosphate deposits in Mazıdağı (Turkey). The sample was crushed, screened and classified using ASTM standard sieves. 150–180 μm particle size was used for the removal of Pb^{2+} ions from aqueous solutions. Chemical analyses of the rock phosphate were carried out by standard gravimetric and volumetric methods and the results are summarized in Table 1.

For the infrared spectroscopy, the phosphate sample was ground to a very fine powder form in an agate mortar for a minimum of 10 min. After drying at 105 °C for 24 h, dilution and homogenization of

Table 1
Chemical composition of rock phosphate.

Constituents	(% wt/wt)
SiO_2	1.73
P_2O_5	5.53
CaO	51.26
MgO	1.35
Fe_2O_3	0.96
Al_2O_3	1.07
F_2	0.33
Loss on ignition	37.73

1.5 mg of rock phosphate and 300 mg KBr were carried out with additional grinding. Purity of the samples before and after adsorption was tested by IR spectral analysis. An IR transmittance spectrum of the ground sample was obtained in the 400–4000 cm^{-1} range with a Perkin Elmer spectrum one FTIR spectrometer.

2.2. Experimental procedure

Lead solutions were prepared by dissolving Pb(NO$_3$)$_2$ analytical grade. Adsorption experiments were carried out in the batch reactors (250 mL Erlenmeyer) containing various amounts of rock phosphate (low-grade) as adsorbent and 100 mL of Pb^{2+} solutions having different concentrations (25, 50, 75 and 100 mg/L) and pH (3–6). In order to investigate the effect of the temperature on the adsorption, four adsorption temperatures (25, 35, 45, and 55 °C) were studied. The suspensions were shaken on an orbital shaker at a constant agitation rate of 200 rpm for different time intervals. Then, the suspensions were filtered and the Pb^{2+} concentration in the filtrate was analyzed using an atomic absorption spectrophotometer (Shimadzu AA-670). The experiments were performed in duplicate and mean values were taken into account.

The removal efficiency of lead was calculated from the equation below;

$$\%\,\text{Removal} = \frac{(C_o - C_e)}{C_o} \times 100. \tag{1}$$

The adsorption capacity of lead was calculated from the following mass balance equation,

$$q_e = \frac{(C_o - C_e)v}{m} \tag{2}$$

where q_e (mg g^{-1}) is the equilibrium adsorption capacity, C_o and C_e are the initial and equilibrium concentrations (mg/L) of Pb^{2+} ions in solution, v (L) is the volume solution and m (g) is the weight of the adsorbent.

3. Results and discussions

3.1. Effect of pH

One of the most critical parameters in the adsorption process of metal ions from aqueous solutions is the pH of the medium. Hence, the effect of initial pH on the uptake capacities of Pb^{2+} on rock phosphate (low-grade) was studied. The pH range studied was between 3 and 6 for initial Pb^{2+} concentration. The reaction temperature was kept at 25 °C and at a constant agitation rate of 200 rpm on a shaker for 2 h in 100 mL Pb^{2+} solutions with a concentration of 50 mg/L. The results are shown in Fig. 1. The adsorption capacity was found to be increased from pH 3 to 5. However, beyond pH 5 no increase was observed. For the subsequent experiments, pH 5 was chosen to avoid metal precipitation at higher pH values.
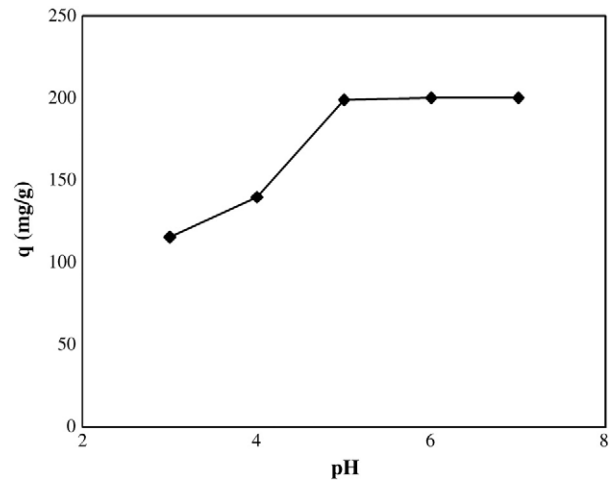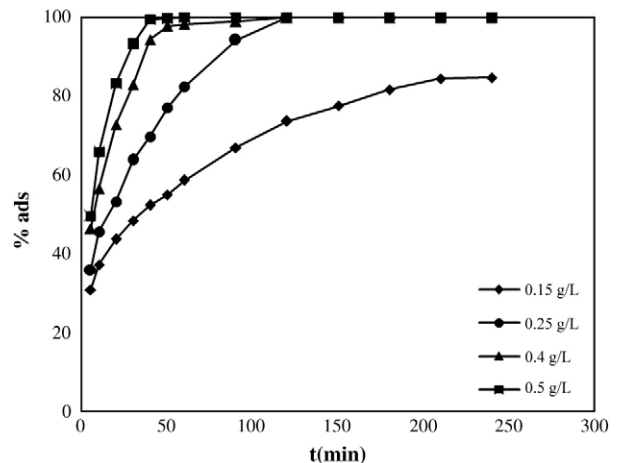

Fig. 1. Effect of pH on Pb^{2+} adsorption (initial Pb^{2+} concentration 50 mg/L, adsorbent dosage 0.25 g/L, T 25 °C).

3.2. Effect of adsorbent dosage

The effect of the adsorbent dosage on the removal of lead ions for various contact times was studied by varying the adsorbent dosage in the range of 0.15–0.5 g/L with 200 rpm stirring speed and at pH 5 in 100 mL Pb^{2+} solutions with a concentration of 50 mg/L. The results are shown in Fig. 2. The percentage adsorption of Pb^{2+} increases with increasing rock phosphate dosage. This increase can be attributed to the increase in the number of adsorption sites. For all subsequent experiments, a 0.25 g/L adsorbent dosage was chosen. Maximum adsorption capacity of rock phosphate was found to be 200 mg Pb^{2+}/g adsorbent.

3.3. Effect of initial concentration of metal ions

The effect of initial Pb^{2+} concentration on the adsorption was investigated by changing the initial Pb^{2+} concentration in the range of 25–100 mg/L under the optimized conditions (pH 5, adsorbent dosage 0.25 g/L, and temperature 25 °C). The results are shown in Fig. 3. The removal of Pb^{2+} was found to be dependent on the initial concentration, the amount adsorbed increasing with an increase in initial concentration. Further, the adsorption is rapid in the early stages and then attains an asymptotic value for larger adsorption time. At low concentration (25 ppm) the ratio of available surface to the initial Pb^{2+} concentration is larger, so the removal becomes independent of initial concentrations.

Fig. 2. Effect of adsorbent dosage on Pb^{2+} adsorption (pH 5, initial Pb^{2+} concentration 50 mg/L, T 25 °C).