Kinetic Studies of Zn(II) Removal from Single and Binary Solutions by Synthetic Hydroxyapatite - Based Nanopowders

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A kinetic study has been carried out with two hydroxyapatite nanopowders to establish the mechanism involved in heavy metals removal from aqueous synthetic solutions. The samples of nanohydroxyapatite have been previously characterized. The first sample represents a pure hydroxyapatite (HAP) nanopowder named HAP-1, and the second sample (HAP-2) consist of a mixture of hydroxyapatite (HAP; $Ca_{10}(PO_4)_6(OH)_2$) and β-tricalcium phosphate (β-TCP; $Ca_3(PO_4)_2$). Batch experiments with single and binary Zn(II) and Pb(II) aqueous solutions have been performed. According to this research study, it was found that the both nanohydroxyapatite samples show good heavy metals adsorption capacity, and selectivity for Pb(II) ions. A more pronounced decreasing of sorption capacity of Zn(II) ions from binary solutions compared to that registered from single heavy metal ion solutions has been observed. From the kinetic point of view, the sorption process can be described for both heavy metals as a pseudo-second-order kinetic process. According to this model, the Zn(II) and Pb(II) sorption can be achieved by chemical reactions between heavy metals and functional groups of adsorbents. The obtained results are indicative of good hydroxyapatite adsorption ability towards Pb(II) and Zn(II) ions.

Keywords: synthetic nanohydroxyapatite, sorption capacity, lead and zinc removal, kinetic studies, kinetic sorption models

The presence of heavy metal ions within the environment has negative consequences to the ecosystems and human health. Heavy metal ions are known to be highly toxic and they are included in the category of toxic pollutants. Numerous industrial effluents loaded with heavy metals are discharged into the environment from industries such as: metal finishing processes, electroplating industry, mining industry, batteries manufacture, inorganic chemical industry, textile industry, paintings, printing and photographic industries, energy industry and extractive hydrometallurgical processes [1-5].

The most common contaminants in the heavy metals category are: Al(III), Cd(II), Co(II), Cr(VI), Cu(II), Hg(II), Zn(II), As (III, V). Technically efficient and economically feasible methods to treat industrial wastewater loaded with heavy metals are needed to avoid water pollution. In function of wastewater characteristics, two types of treatment categories are applied. In the first category, named conventional treatment methods the followings, are included: chemical precipitation, ion-exchange, adsorption, chemical reduction, flocculation, filtration, solvent extraction, evaporation, electrodialysis, and membrane separation processes [6-9]. All of these technologies have advantages and disadvantages (high operating costs, but also the fact that some of them lead to heavy metal sludge which either will be stored and thus water pollution turns into a soil pollution with waste, either requires further processing) [10-12]. Unconventional treatment methods are represented by bioremediation methods (also called environmental biotechnologies). In the category of bioremediation methods can be included: bioaccumulation, biosorption and phytoremediation. Among the main advantages of bioremediation methods are the following: lack of secondary pollution, environmentally friendly and low costs [13].

Hydroxyapatite natural and synthetic is one of the most common used as heavy metals removal material due to the fact that it shows high capacity for ion exchange with heavy metal ions owing to its unique crystal structure and composition. The crystal structure $(A_4^{I})(A_6^{II})(BO_4)_6(X_2)$ of HAP allows a high degree of disorder structural due to multiple chemicals substitutions. Consequently, heavy metal ions such as Pb(II) and Zn(II) can substitute Ca(II) from HAP. The main mechanisms determined to take place in heavy metals removal by HAP are: formation of a pyromorphite phase after apatite dissolution (formation of insoluble compounds), adsorption, surface complexation and ion exchange [5, 9, 10].

Kinetic studies of heavy metal ions removal from solutions give insights into the mechanism and the rate determine step of the process of pollutants removal and facilitate the engineering process. Different kinetic models are usually investigated for their suitability to describe the rate of heavy metal ions removal process, the most common ones are (i) pseudo first-order kinetic model, (ii) pseudo second-order kinetic model, and (iii) intra-particle diffusion model [14-19].

To examine the mechanism of heavy metals removal by HAP and the rate limiting steps, the kinetic data of Zn(II) and Pb(II) removal were modeled.

Experimental part

Materials

Two nano-HAP powders previously prepared and characterized by XRD, SEM and BET methods, as reported in previous paper [20] have been used as heavy metals removal materials. Stock solutions of 1000 mg Zn(II)/L and 1000 mg Pb(II)/L have been prepared from zinc nitrate (Merck, Germany) and lead nitrate (Merck, Germany). The stock solutions were diluted to prepare single and binary heavy metals solution with tested concentrations.

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Sorption studies

Experiments in batch mode were performed at room temperature in duplicate to determine the sorption capacity of the sorbents tested. Three sets of experiments were performed.

Zn(II) and Pb(II) ions concentration in the initial solutions and after the sorption experiments has been determined by atomic absorption spectrometry on a Contra®300 AAS Atomic Adsorption Spectrometer. All the sorption experiments have been performed on a GFL Shaker 3015 at 150 rpm.

The optimum conditions of the Zn(II) and Pb(II) removal process by adsorption onto HAP samples have been previously determined [20]. These are: solution natural *p*H (6 – 6.3 depending of the solution's composition) and 240-300 min as contact time.

The sorption capacity and the amount of Zn(II)/Pb(II) ions adsorbed by nano-HAP particles (mg/g) were determined by the following equation:

$$Q = \frac{(C_i - C_e) \times V}{m} \quad (1)$$

where Q designates heavy metal ions uptake (mg/g),

C_i represents the pollutant's concentration in the initial solution (mg/L),

C_e is the pollutant's concentration in the solution at equilibrium (mg/L),

V – solution's volume (L), and

m - mass of nano-HAP used (g).

HAP nanopowders were investigated into the removal process of Zn(II) and Pb(II) from single and binary aqueous solutions. The batch tests have been performed in order to assess the mechanism involved in the Zn(II) and Pb(II) removal by nano-HAP samples.

The experiments were carried out at the following operating conditions: 50 mL heavy metal ions solution, 50 mg of nano-HAP, room temperature, 150 rpm speed rotation, for time varied between 5 to 240 min and *p*H 6 - 6.3. The monocomponent solutions with concentrations: 100.82 mg Zn(II)/L and 107 mg Pb(II)/L respectively, and binary solutions with concentrations: 94.7 mg Zn(II)/L and 100.53 mg Pb(II)/L have been used in kinetic study.

Results and discussions

The mechanism of any sorption process is controlled by kinetic models. Therefore, kinetic studies should be performed to determine the kinetic model characterizing the Zn(II) and Pb(II) sorption process onto nano-HAP. For this purpose, experimental data were analyzed using three of the most commonly used kinetic models. These are the pseudo-first-order kinetic model, the pseudo-second-order kinetic model and intraparticle diffusion. These theoretical mathematically kinetic models have been applied to experimental data in order to find the models that adequately describe the kinetic data related to the analyzed sorption process.

The pseudo-first-order kinetic model is based on the assumption that the rate of the adsorption process is proportional to the number of free active centers on the surface of the sorbent. This model is expressed in the form of the Lagergren equation:

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \quad (2)$$

where: k_1 is the rate constant of the pseudo-first-order sorption process (min^{-1}) and Qe, Qt represent the equilibrium sorption capacity and the sorption capacity at time t (mg/g).

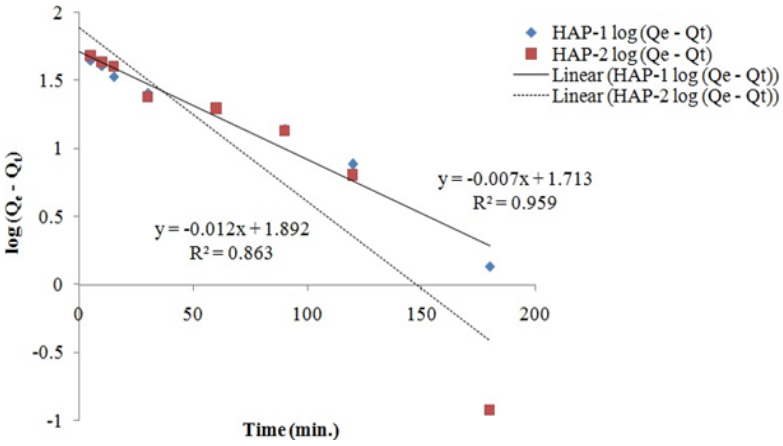

Fig. 1. Pseudo-first-order kinetics of Zn(II) sorption on HAP samples

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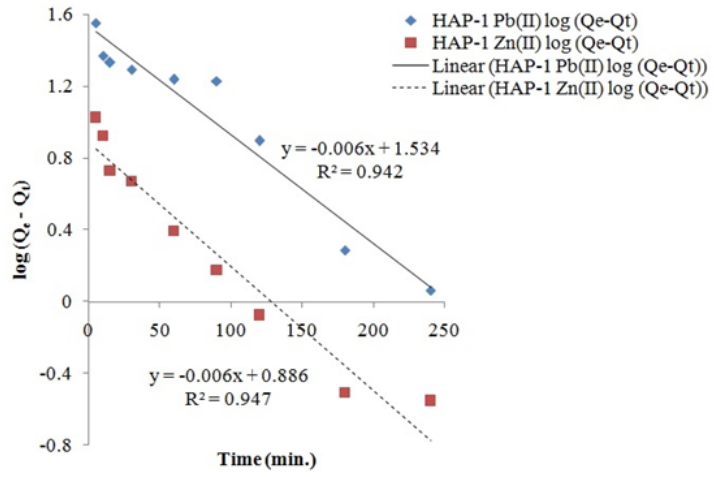

Fig. 2. Pseudo-first-order kinetics of Zn(II) and Pb(II) sorption onto HAP-1 sample

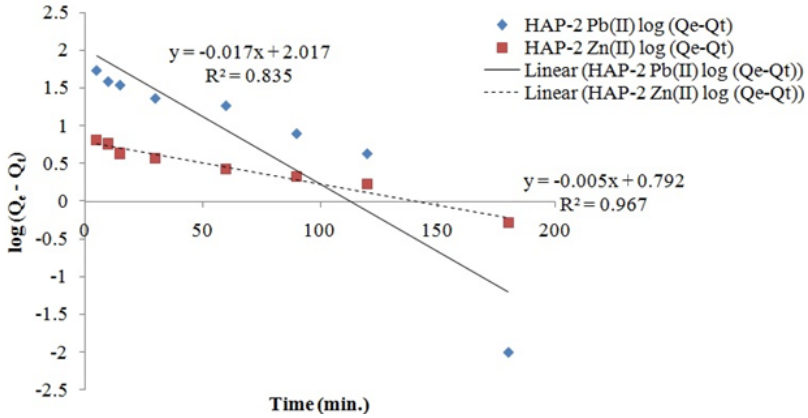

Fig. 3. Pseudo-first-order kinetics of Zn(II) and Pb(II) sorption onto HAP-2 sample

The linear form of the Lagergren equation is:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} \cdot t \qquad (3)$$

where: k_1 is the rate constant of the pseudo-first-order sorption process (min^{-1}) and Qe, Qt represent the equilibrium sorption capacity and the sorption capacity at time t (mg/g).

From the slope of the straight line and the intersection of the straight lines in the graphical representations log (Q_e -Q_t) versus t (figs. below) we calculate k_1, the equilibrium sorption capacity (Q_e) and the correlation coefficient R^2.

The pseudo-second-order kinetic model is mathematical expressed using the equation Ho:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \qquad (4)$$

where k_2 is the rate constant of the pseudo-second-order sorption process (g/mg·min).

The experimental data of Zn(II) and Pb(II) sorption process onto nano-HAP have been fitted with pseudo-second-order kinetic expression (figures below).

The kinetic model of the intraparticle diffusion is mathematically expressed by the equation:

$$Q_t = k_i t^{0.5} \qquad (5)$$

where k_i is the intraparticle diffusion rate constant ($mg/g \cdot min^{0.5}$).

From the graphical representations shown in figures 7-9, it can be observed that the kinetic model of the intraparticle diffusion was not the only rate-limiting step of the sorption process of Zn (II) and/or Pb (II) on HAP, because two straights can be drawn through these points. Thus, it can be said that the sorption process monitored comprises of two phases. The first, phase indicates that mass transfer resistance was limited to the initial stages of adsorption. The initial stages of adsorption process are through the boundary layer diffusion of Zn(II)/Pb(II) ions from the bulk solution onto the external surface of HAP, whereas the later stages of adsorption are due to the intra-particle diffusion of the metals ions [21]. Since the straight line of the second phase of adsorption was not passing through the origin, it can be concluded that intra-particle diffusion was not the only rate-limiting step in case of Zn(II) and Pb(II) removal process. Therefore, the adsorption data were further examined using Lagergren's pseudo-first-order and pseudo-second order kinetic models to evaluate the rate-limiting step.

The data presented in the figures above were used for calculating the kinetic model parameters and for calculating the correlation coefficient (R^2). The values of these parameters are shown in the table 1.

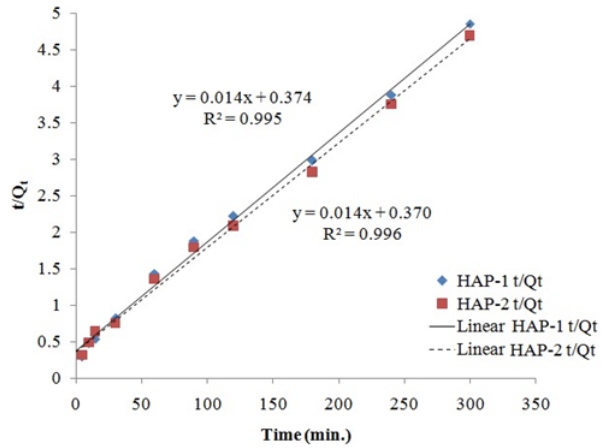

Fig. 4. Pseudo-second-order kinetics of Zn(II) sorption on various samples of HAP

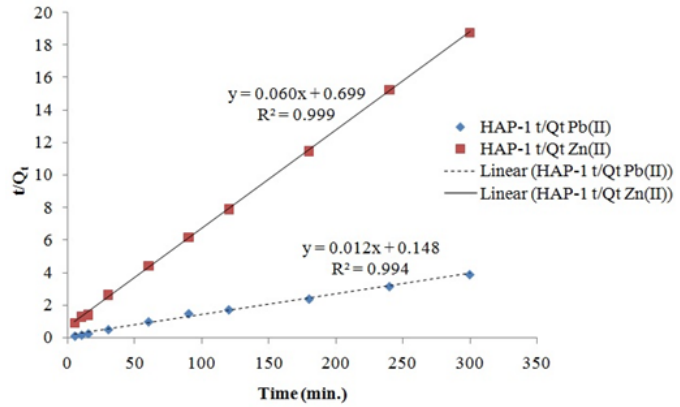

Fig. 5. Pseudo-second-order kinetics of Zn(II) and Pb(II) sorption on HAP-1

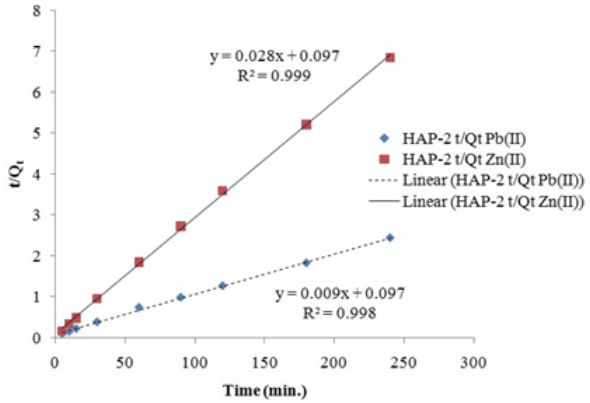

Fig. 6. Pseudo-second-order kinetics of Zn(II) and Pb(II) sorption on HAP-2

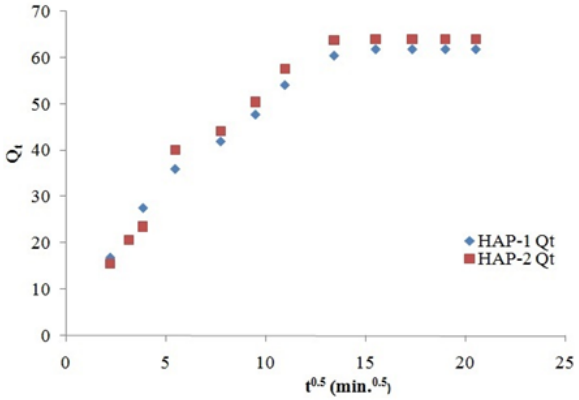

Fig. 7. Intraparticle diffusion kinetic of the Zn(II) sorption process on various HAP samples

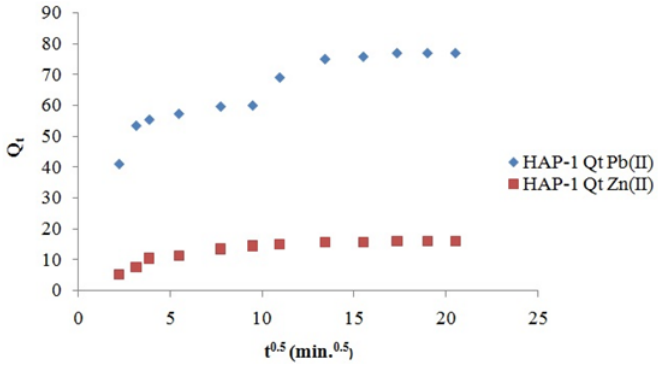

Fig. 8. Intraparticle diffusion kinetic of the Zn(II) and Pb(II) sorption process on HAP-1

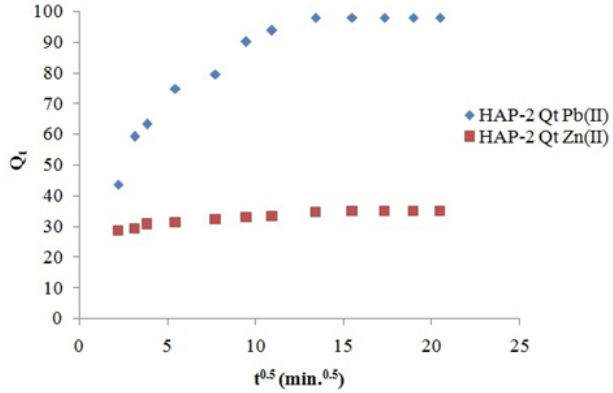

Fig. 9. Intraparticle diffusion kinetic of the Zn(II) and Pb(II) sorption process on HAP-2

Table 1

THE KINETIC PARAMETERS SPECIFIC FOR Zn(II) AND Pb(II) SORPTION ONTO HAP-BASED MATERIALS

Sample	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
	k_1 (min^{-1})	Q_e (mg/g)	R^2	k_2 (g/mg·min)	Q_e (mg/g)	R^2
Zn(II) sorption from single solutions						
HAP-1	0.0276	51.65	0.959	$5.2406 \cdot 10^{-4}$	71.43	0.995
HAP-2	0.0161	78	0.863	$5.2973 \cdot 10^{-4}$	71.43	0.996
Zn(II) sorption from binary solutions						
HAP-1	0.0138	7.7	0.947	$5.1503 \cdot 10^{-4}$	16.67	0.999
HAP-2	0.0115	6.2	0.967	$7.7815 \cdot 10^{-2}$	35.71	0.999
Pb(II) sorption from binary solutions						
HAP-1	0.0138	34.24	0.942	$9.7297 \cdot 10^{-4}$	83.33	0.994
HAP-2	0.0391	104	0.835	$9.0000 \cdot 10^{-4}$	111.11	0.998

The data presented in the table above show that the values of the correlation coefficient (R^2) was higher for pseudo-second order kinetic model than pseudo-first order kinetic model. Futthermore, the values of sorption capacity determined from pseudo-second-kinetic model are close to the values of sorption capacity determined experimental. This indicates that the Zn(II) and Pb(II) sorption process on various samples of HAP-based materials can actually be described using the pseudo-second-order kinetic model. Consequently, the rate determining step is chemical sorption [22-25]. Thus, the process of Zn(II) and Pb(II) from single and binary solutions can be described as chemosorption.

The experimental data obtained lead to the conclusion that the tested HAP samples can be successfully used in the process of removing zinc ions from synthetic solutions and actual wastewater.

Conclusions

Two HAP based materials have beed used to determine the mechansim involved in Zn(II) and Pb(II) removal from single and binary aqueous solutions. One of the adsorbent materials consist of pure nano-HAP and the second is a biphasic calcium phosphate (BCP) ceramics consists of a mixture of hydroxyapatite (HAP) and β-tricalcium phosphate (β-TCP). This material combines physico-

chemical properties of these two components: a good solubility of β-TCP leading to obtain local supersaturation in calcium and phosphate ions along with a good nucleation capacity of HAP. The sorption capacity of HAP samples depends on the crystallinity degree, particle's size and specific surface. It has been observed that the content of β-TCP doesn't have a negative effect on sorption capacity of HAP sample.

The results indicated the better applicability of pseudo-second-order kinetic model for both heavy metal ions removed by HAP-based materials. This suggested that, the Zn(II) and Pb(II) sorption is controlled by chemical reactions between heavy metals and functional groups of adsorbents.

The values of sorption capacity revealed using of nano-HAP powders in heavy metals removal from synthetic and real wastewater.

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