Application of Nano-hydroxyapatite Synthesized by Microwave in Efficient Removal of Lead(II) and Copper(II) from Aqueous Solutions

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Nano-hydoxyapatite was prepared using a rapid microwave method as an effective sorbent for lead(II) and copper(II) removal from aqueous solutions. The surface of the produced nano-hydoxyapatite has a porous structure and the specific surface area according to the BET model in value of 88.75 mg/g. Batch experiments revealed that removal ration increased in the order of lead (96.56 %), and copper (40.69%) in mixed solutions with the initial solution with concentration 100 mg Cu(II)/L amd 100 mg Pb(II)/L. The maximum adsorption capacity of lead and copper determined were 99.94 mg/g and 40.04 mg/g. The results of this research study can lead to the conclusion that nano-hydroxyapatite can be used as a cost-effective material for the removal of lead and copper from binary aqueous solutions and wastewater.

Keywords: lead and copper removal, nano-hydroxyapatite, microwave heating

One of the important environmental problems is water contamination with heavy metals arising from tannery, fertilizers industry, textile industries, metal plating, mining industries, batteries production, pigment and dyes industries, glass industry, electrochemical processes, pesticides and wood preservatives production [1]. Their extreme toxicity even at low levels, their tendency to accumulate in food chain and the fact that they are not biodegradable are the main issues related to heavy metals [2]. The main heavy metals which pose human health threats are lead, cadmium, mercury, copper and arsenic. All these metals have been extensively examined and their effects on human health are regularly reviewed by international organizations such as the World Health Organization (WHO) [3]. Thus, lead ions cause of nephrotoxicity, hypertension and neurotoxicity by their effect on the physiological and biochemical processes of human organisms. Lead can substitute calcium and therefore it is found in bones. Children and elders are the most susceptible to lead poisoning [4]. Copper can be accumulated in liver cells and determine hemolytic crisis and neurological disturbances [5]. Consequently, these metals have to be eliminated from wastewaters and waste before to be discharge into environment.

The main traditional methods used to remediate heavy metals polluted waters are chemical precipitation, ion exchange, sorption, membrane filtration, flotation, reverse osmosis, and electrochemical processes [6, 7]. From these technologies, adsorption onto solid materials has been used as one of the most suitable method to remove heavy metals from wastewater and aqueous solutions. Activated carbons, fishbone, zeolites, clays, composite materials, starch, chitosan, oxides and hydroxides, fly ash, phosphate, cellulose, carbon nanotubes, biomass-derived sorbents have been used for the removal of heavy metals from polluted environments [8-10].

Hydroxyapatite has obtained an increasing attention in the past years as an efficient material for the removal of heavy metals from wastewaters [9]. Its characteristics such as large specific area, high thermal and chemical stability and high ionic exchange capacity recommend to be used for remediation of heavy metals polluted environments. Natural and synthetic hydroxyapatite (HAP) can be used for this purpose. Hydroxyapatite has been synthesized in the laboratory to avoid depletion of its natural resources. Chemical precipitation [11], hydrothermal synthesis [12], sol-gel methods [13], multiple cross-linked emulsion techniques [14], biomimetic deposition techniques [15], electrodeposition [16], synthesis in the ultrasonic field [17], microwave assisted synthesis [18, 19] have been involved in the nano- and micrometric HAP particles synthesis. Microwave synthesis has as main advantages the reduced synthesis time, it not involves the use of solvent being considered as a *greener* synthesis method, and it can be used to obtain nanoparticles with controlled shape and particle size. As a result, microwave synthesis is considered as a rather promising method to obtain numerous substances and materials. Our recent research studies were focused on the synthesis of hydroxyapatite (HAP) granules in presence of microwave field from $Ca(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$ as raw materials [18, 19]. The porous HAP granules obtained by microwave assisted synthesis have been employed in the removal of lead and copper removal from single synthetic aqueous solutions [18, 19].

It is well known that wastewaters are multi-component systems and the competition between their components can reduces HAP heavy metals removal efficiency. Therefore, the aim of this research study is to investigate the retention od Pb(II) and Cu(II) in aqueous solution by HAP in binary-metal systems.

Experimental part

Materials and testing equipments

Porous HAP granules were obtained according to a method reported in our previous research studies [18, 19]. 1000 mg/L stock Pb(II) solution was prepared by dissolving 1.5986 g of $Pb(NO_3)_2$ (Merck) in 1L distilled water, and 1000 mg/L Cu(II) stock solution was prepared by dissolving 3.8020 g $Cu(NO_3)_2 \cdot 3H_2O$ (Merck) in 1L distilled water. The required concentration of Pb(II) and Cu(II) binary solutions

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were obtained by serial dilution of 1000 mg/L Pb(II) and Cu(II) solutions. 25% NH_3 solution (NH_4OH), 63% HNO_3 and 0.1M HNO_3 solutions analytical grade, Fluka origin were used for *p*H adjustment. The initial metal ions concentration and the remained concentration after the sorption on HAP were determined by atomic absorption spectrometry by the use of ContraAAS®300 Atomic Adsorption Spectrometer. The two phases (solid – HAP and liquid – binary synthetic solutions) were put in contact by the use of a GFL Shaker 3015 at 150 rpm. The solution pH was determined with an Agilent 3200 laboratory pH-meter.

Sorption experiments

Sorption batch experiments were performed to test sorption capacity of HAP particles in the removal of Pb(II) and Cu(II) from binary aqueous solutions. Experiments were performed by diluting the stock solutions of Pb(II) and Cu(II) to desired concentrations.

The effect of the contact time on the sorption of Pb(II) and Cu(II) ions was conducted using 0.05 g of HAP with 50 mL of Pb(II) and Cu(II) ions solution at room temperature (21 ± 2°C). The contact time varied between 5 and 600 min. The initial *p*H was other parameter that was investigated. The *p*H range studied was 2-6. HAP was stirred with the Pb(II) and Cu(II) ions solution at 150 rpm for 600 minutes to reach the equilibrium.

The amount of Pb(II) and Cu(II) ions adsorbed by HAP particles (mg/g), and the removal efficiency (%) were calculated using eqs. (1) and (2).

$$Q=\frac{(C_i-C_f)\cdot V}{m} \qquad (1)$$

where Q represents Pb(II)/Cu(II) uptake (mg/g), C_i is the concentration of Pb(II)/Cu(II) ions in the initial solution (mg/L), C_f is the concentration of Pb(II)/Cu(II) ions remaining in solution at various times (mg/L), V - volume of the solution (L) and m - mass of HAP used (g).

$$\eta=\frac{(C_i-C_f)}{C_i}\cdot 100 \qquad (2)$$

where η is removal efficiency (%), C_i represents the concentration of Pb(II)/Cu(II ions in the initial solution (mg/L), C_f - the concentration of Pb(II)/Cu(II ions remaining in solution at various times (mg/L).

Results and discussion

Effect of pH on Pb(II) and Cu(II) removal process by HAP

Industrial effluents and wastewater with heavy metals content are generally known to have different *p*H values in function of the type of industrial activities. Consequently, there is necessary to perform studies related to identify of the *p*H effect on heavy metal ions adsorption by HAP or other kind of sorbents.

The effect of *p*H on HAP sorption capacity was studied and evaluated by using metal ion solutions adjusted to pH 2.0-6.0. The *p*H > 6.0 was excluded due to the possible precipitation of Pb(II) and Cu(II) as hydroxide species. The selection of acidic solutions is mainly aimed due to the possible release of industrial effluents with this *p*H range.

Figures 1-5 represent the determined metal sorption capacity of Pb(II) and Cu(II) (mg/g) by HAP in function of *p*H value.

The results presented in figures 1-5 show that Pb(II) adsorption on HAP from binary solution is not dependent by *p*H value, while Cu(II) adsorption on HAP shows a slightly dependence by *p*H value. Therefore, the next experiments were performed at *p*H solutions value without changes to acid or basic values.

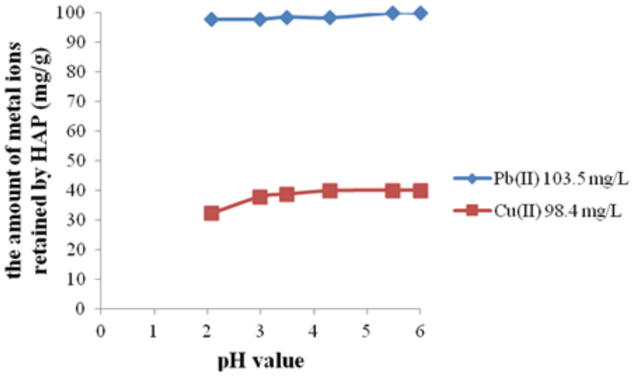

Fig 1. Effect of *p*H on retained amount (mg/g) of Pb(II) and Cu(II) by HAP from binary solution with 103.5 mg/L Pb(II) and 98.4 mg/L Cu(II)

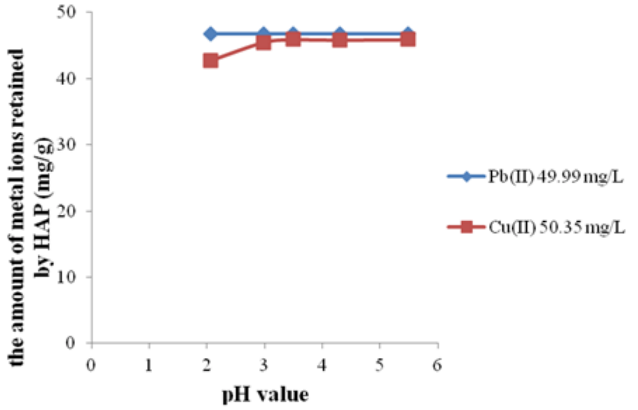

Fig 2. Effect of *p*H on retained amount (mg/g) of Pb(II) and Cu(II) by HAP from binary solution with 49.99 mg/L Pb(II) and 50.35 mg/L Cu(II)

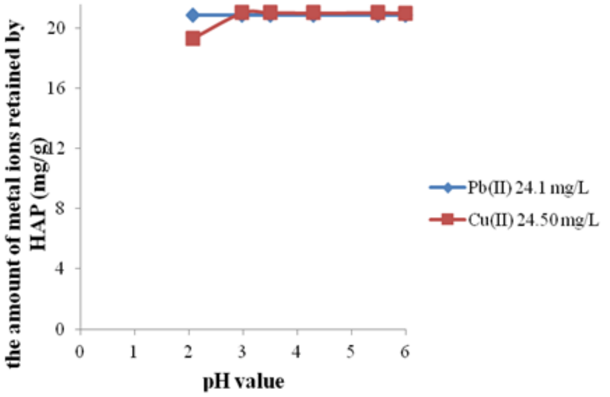

Fig 3. Effect of *p*H on retained amount (mg/g) of Pb(II) and Cu(II) by HAP from binary solution with 24.1 mg/L Pb(II) and 24.5 mg/L Cu(II)

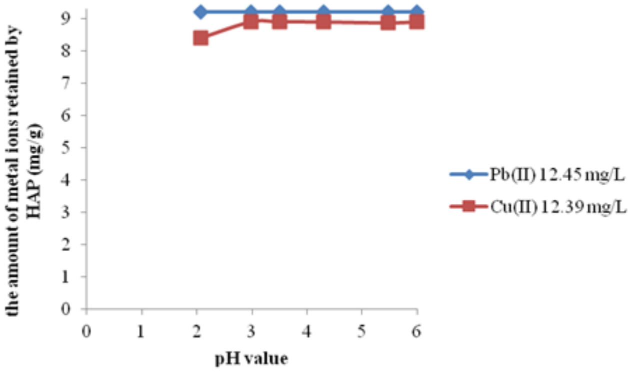

Fig 4. Effect of *p*H on retained amount (mg/g) of Pb(II) and Cu(II) by HAP from binary solution with 12.45 mg/L Pb(II) and 12.39 mg/L Cu(II)

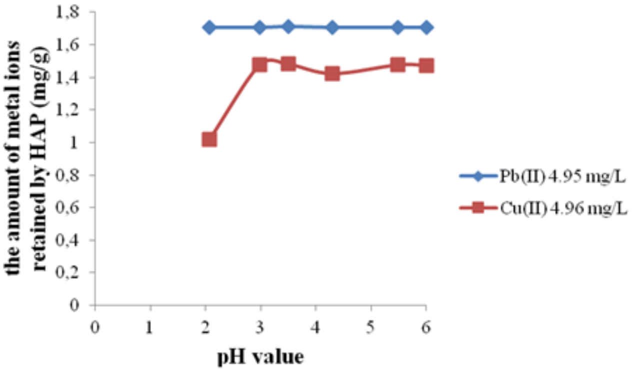

Fig 5. Effect of *p*H on retained amount (mg/g) of Pb(II) and Cu(II) by HAP from binary solution with 4.95 mg/L Pb(II) and 4.96 mg/L Cu(II)

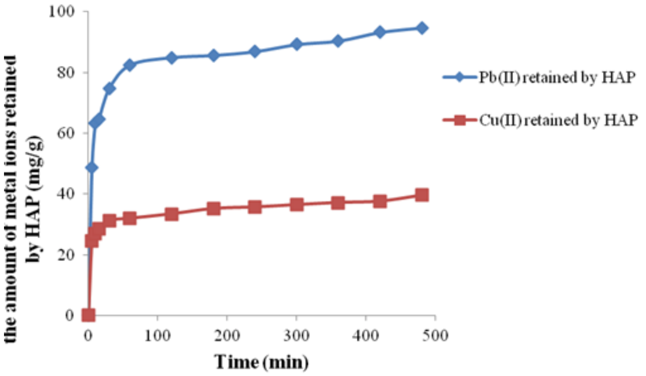

Fig 6. Effect of time on retained amount (mg/g) of Pb(II) and Cu(II) by HAP from binary solution with 103.50 mg/L Pb(II) and 98.40 mg/L Cu(II)

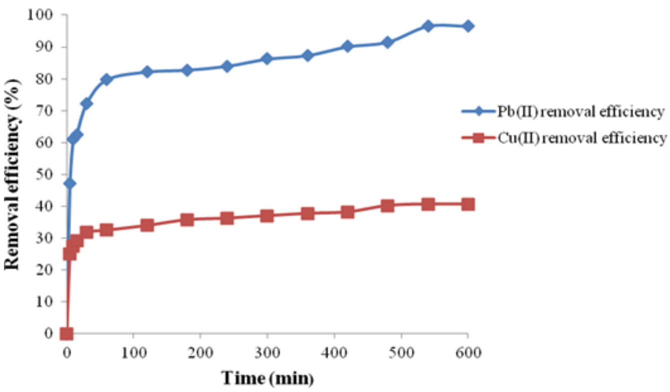

Fig 7. Effect of time on Pb(II) and Cu(II) removal efficiency by HAP from binary solution with 103.50 mg/L Pb(II) and 98.40 mg/L Cu(II)

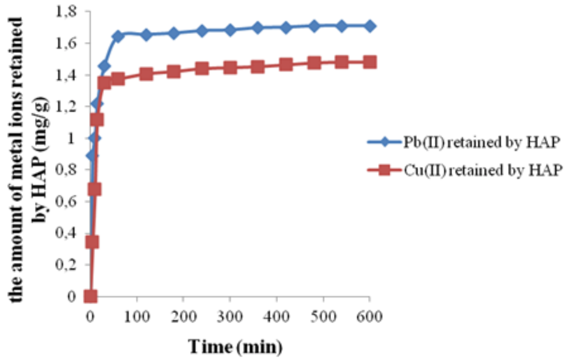

Fig 8. Effect of time on retained amount (mg/g) of Pb(II) and Cu(II) by HAP from binary solution with 4.95 mg/L Pb(II) and 4.96 mg/L Cu(II)

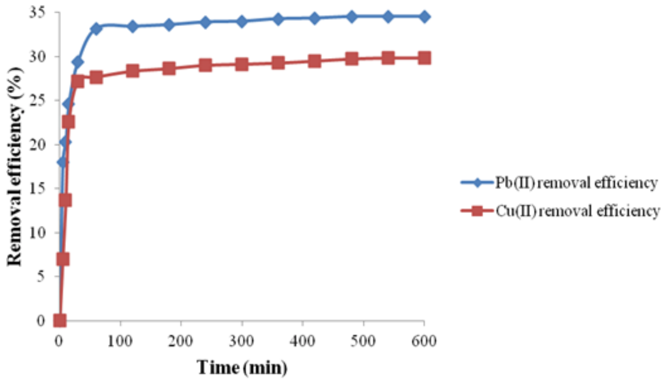

Fig 9. Effect of time on Pb(II) and Cu(II) removal efficiency by HAP from binary solution with 4.95 mg/L Pb(II) and 4.96 mg/L Cu(II)

Effect of time on Pb(II) and Cu(II) removal process by HAP

The contact time is one of the important parameters when dealing with economical evaluation and practical application in water treatment processes [20]. Consequently, the effect of contact time on metal uptake by HAP and removal efficiency was also studied and evaluated by batch experiments. The selected shaking time intervals (5, 10, 15, 30, 60, 120, 180, 240, 300, 360, 420, 480, 540, 600 min) were considered to evaluate the effect of contact time on adsorption capacity and removal efficiency. The results of this study are presented in the followings figures.

It is evident from these figures, that both the amount of metal retained by HAP and removal efficiency of the two evaluated metal ions exhibited a gradual increase with increasing the contact time. The maximum values of the amount of Pb(II) and Cu(II) retained by HAP named sorption capacity are 99.94 and 40.04 mg/g. These values indicate a good sorption capacity and selectivity of HAP to Pb(II) ions. Other conclusion that can be drawn from these results is that the removal efficiency increases with the increasing contact time, and the time to reach the equilibrium is 540 min. Therefore, Pb(II) and Cu(II) removal process by HAP from binary aqueous solutions can be considered a fast process.

Effect of HAP dose on Pb(II) and Cu(II) removal process

The effect of HAP dose on the metal sorption capacity values was also studied as an important parameter to identify the relationship between metal sorption capacity and adsorbent mass. Solution with 49.99 mg/L Pb(II) and 50.35 mg/L Cu(II) was chosen for this study.The contact time was 600 min, the solution volume was 50 mL, and HAP dose varied between 0.01 and 0.2 g. The results of this study are summarized in table 1.

From table 1 it can be seen that the metal adsorption capacity values of Pb(II) and Cu(II) are inversely proportional to the mass of HAP.

Adsorption isotherm

A relationship between the amount of adsorbed metal ion on the surface of adsorbent and the concentration of metal ion in solution at the equilibrium is provided by adsorption isotherm [20]. Langmuir and Freundlich isotherms are used to describe the distribution of metal ions between liquid and solid phases. The Langmuir equation is frequently used to give the adsorption equilibrium, and it assumes that the metal uptake process takes place on the surface of adsorbent in a homogeneous monolayer distribution without any type of interaction between adsorbed ions [20]. The Langmuir isotherm

Table 1
THE EFFECT OF HAP DOSE ON Pb(II) AND Cu(II) REMOVAL PROCESS

HAP dose (g)	Pb(II) retained by HAP (mg/g)	Cu(II) retained by HAP (mg/g)
0.01	46.7901	46.177
0.02	46.7891	46.077
0.05	46.7503	45.9171
0.1	45.2134	44.5631
0.2	44.1101	43.1102

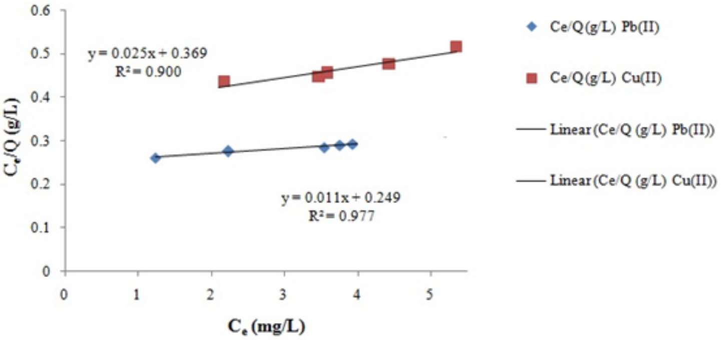

Fig 10. Langmuir linearised sorption isotherms of lead and copper in binary-metal systems

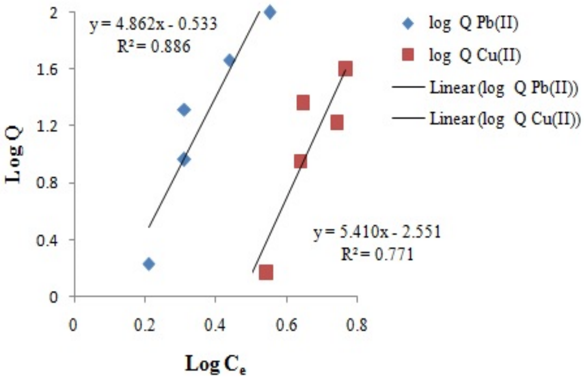

Fig 11. Freundlich linearised sorption isotherms of lead and copper in binary-metal systems

Table 2
LANGMUIR AND FEUNDLICH PARAMETERS FOR Pb(II) AND Cu(II) SORPTION BY HAP FROM BINARY-METAL SYSTEMS

Metal ion	Langmuir parameters			Freundlich parameters		
	Q_{max} (mg/g)	b (L/mg)	R^2	K_F (mg/g)	n	R^2
Pb(II)	90.90	22.64	0.977	0.289	0.21	0.886
Cu(II)	40	14.67	0.900	0.123	0.18	0.771

allows the calculation of the adsorption capacities and Langmuir constant by the following linearized eq. (3).

$$\frac{C_e}{Q_e}=\frac{1}{Q_{max}\cdot b}+\left(\frac{1}{Q_{max}}\right)\cdot C_e \qquad (3)$$

where Q_e – cantitatea de ioni metalici adsorbitã pe unitatea de masã a adsorbentului, C_e - the equilibrium concentration of Pb(II)/Cu(II) (mg/L); Q_{max} (mg/g) and b (L/mg) are the Langmuir model parameters related to the maximum sorption capacity and energy of sorption, respectively. [21].

The Freundlich isotherm is one of the most frequently used models for interpretation of the adsorption process as well as the determination of adsorption parameters [20]. The widely used empirical Freundlich equation based on a heterogeneous surface is given by eq. (4) [22].

$$Q=K_F\cdot C_e^{1/n} \qquad (4)$$

where K_F is Freundlich constant represented sorption capacity and n is Freundlich constant that show sorption intensity.

After logarithmation, the equation (3) will be:

$$\log Q=\log K_F+\frac{1}{n}\log C_e \qquad (5)$$

The Langmuir and Freundlich linearized isotherms for Pb(II) and Cu(II) sorption on HAP are presented in figures10 and 11. These have been used to determine the Langmuir and Feundlich parameters presented in table 2.

The linearity of the plots *Ce/Q*e versus *Ce* (fig. 10) showed that Langmuir model adequately described the sorption data for the metal ions in binary-systems. Furthermore, the values of correlation coefficient (R^2) are much closer to the value 1 for Langmuir equation for both heavy metals than those for Freundlich equation. Thus, it can be concluded that Langmuir isotherm could be considered as a better fitting model than Freundlich for Pb(II) and Cu(II) sorption on HAP nanoparticles indicating the applicability of a monolayer coverage of the metal ions on the surface of HAP nanoparticles.

Adsorption kinetic

The pseudo-first order, pseudo-second order and intraparticle diffusion models were used to determine the kinetic mechanism of the Pb(II) and Cu(II) from binary systems adsorption process.

The pseudo-first-order model presented by Lagergren equation (6) considers that the rate of adsorption on sorbent is proportional to the number of active sites available onto adsorbent [23].

$$\frac{dQ_t}{dt}=k_1(Q_e-Q_t) \qquad (6)$$

where: Q_e, Q_t are the sorption capacities at equilibrium and at time t (mg/g), and k_1 is the rate constant of pseudo-first order sorption (min^{-1}).

The linear form of the Lagergren model as follows (equation 7) was used to analyze the kinetic data:

$$\log(Q_e-Q_t)=\log Q_e-\frac{k_1}{2.303}\cdot t \qquad (7)$$

where Q_e and Q_t represent the amount of Pb(II) and Cu(II) adsorbed onto HAP (mg/g) at equilibrium and at time t, respectively and k_1 is the rate constant of first-order sorption (min^{-1}). The values of rate constant, k_1 and correlation coefficient, R^2 for Pb(II) and Cu(II) sorption were determined from the slope and intercept of the liner plot ofc log(Q_e-Q_t) versus t (fig. 12).

The second-order model [24] represented by the equation (7) is based on the assumption that adsorption follows a second order chemisorption:

$$\frac{t}{Q_t}=\frac{1}{k_2Q_e^2}+\frac{t}{Q_e} \qquad (7)$$

where: k_2 is the rate constant of second-order adsorption (g/mg·min). The values of k_2 and Qe were calculated from the linear plot of t/Qt versus t (fig. 12). The results have been used to determine the applicability of the second-order kinetic model to the experimental data.

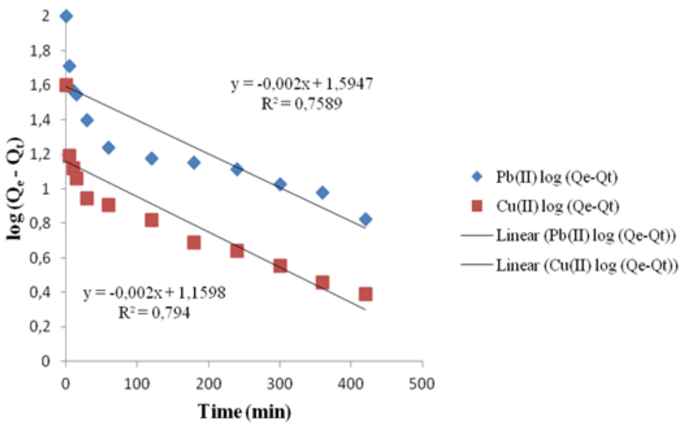

Fig. 11. Pseudo-first order sorption kinetics of Pb(II) and Cu(II) from binary aqueous system onto HAP

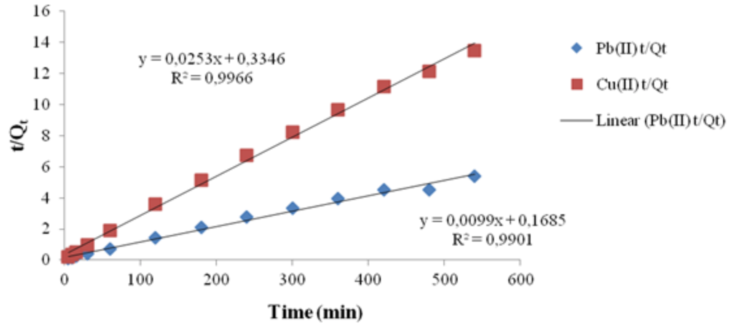

Fig. 12. Pseudo-second order sorption kinetics of Pb(II) and Cu(II) from binary aqueous systems onto HAP

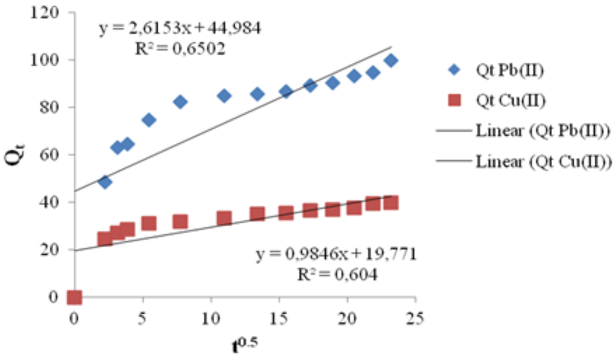

Fig. 13. Intraparticle diffusion sorption kinetics of Pb(II) and Cu(II) onto HAP

Table 3
THE RATE CONSTANT AND R^2 CORRELATION COEFFICIENT VALUES FOR Pb(II) AND Cu(II) SORPTION ONTO HAP

Heavy metal ions	Pseudo-first order sorption		Pseudo-second order sorption		Intraparticle difusion	
	k_1 (min^{-1})	R^2	k_2 (g/mg·min)	R^2	k_i (mg/mg·$min^{0.5}$)	R^2
Pb(II)	$4.606 \cdot 10^{-3}$	0.758	$4.8215 \cdot 10^{-4}$	0.990	2.615	0.650
Cu(II)	$4.606 \cdot 10^{-3}$	0.794	$1.8713 \cdot 10^{-3}$	0.996	0.984	0.604

To elucidate the diffusion mechanism was also applied the equation characteristic to the intraparticle diffusion model (8) [25]:

$$Q_t = k_i t^{0.5} \qquad (8)$$

*where k_i is intra*particle diffusion rate (mg/g·min). The k_i is the slope of straight-line portions of the plot of Q_t against $t^{0.5}$. Intraparticle diffusion kinetic for PbII) and Cu(II) sorption on HAP is presented in figure 13.

The sorption constants and the correlation coefficients for all three models used are reported in the table 3.

From table 3 (R^2=0.990 for Pb(II) and 0.996 for Cu(II)) it can be concluded that pseudo-second-order model is in better agreement with experimental data regarding the kinetics of Pb(II) and Cu(II) ions sorption on HAP compared to pseudo-first-order and intraparticle diffusion. The pseudo-second-order kinetic assumes that the rate determining step is chemical adsorption and not physical sorption and the mass transfer.

Conclusions

The HAP prepared by the use of a rapid microwave method was found to be useful as an adsorbent for the removal of Pb(II) and Cu(II) ions from binary aqueous solution. Optimum removal for both metal ions was obtained at pH of synthetic solution and a contact time of 540 min was utilized for equilibrium removal. Among the adsorption isotherm model tested, the Langmuir model gave the best fit to the experimental data for both metal ions, indicating the applicability of a monolayer coverage of the metal ions on the surface of HAP nanoparticles. The kinetic data followed the pseudo-second order kinetic, thus Pb(II) and Cu(II) sorption onto HAP can be described as chemisorptions. The value of sorption capacity recommends HAP as an effective adsorbent in Pb(II) and Cu(II) removal from aqueous solutions and wastewater, and the selectivity of this sorbent follows the series Pb(II) > Cu(II).

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