Simultaneous Removal of Lead(II), Nickel(II), Zinc(II) and Copper(II) from Aqueous Solutions by Nano-hydroxyapatite Synthesized by Microwave Field

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In the present work, nano-hydroxyapatite (nano-HAP) prepared in microwave field was applied to remove lead(II), nickel(II), zinc(II) and copper(II) from polycationic aqueous solutions. Optimum adsorption conditions were evaluated using batch experiments. Effect of various physicochemical parameters such as: pH, contact time, and initial ion concentration on adsorption of metal ions onto nano-HAP was evaluated. Batch experiments revealed that removal ration decreased in the order: 87.1% for Pb(II), 44.66% for Zn(II), 20.39% for Cu(II) and 19.97% for Ni(II) in mixed solutions with the initial solution with concentration 90.72 mg Pb(II)/L, 92.32 mg Zn(II)/L, 108.8 mg Cu(II)/L, and 99.39 mg Ni(II)/L. The maximum adsorption capacity of lead, nickel, zinc and copper determined were 79.02 mg/g, 19.85 mg/g, 41.23 mg/g and 22.18 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, nickel, zinc and copper from polycationic aqueous solutions.and wastewater. The selectivity of this material follows the series: Pb(II) > Zn(II) > Cu(II) > Ni(II).

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

The presence of heavy metals such as lead, nickel, zinc and cooper in wastewater is of prime concern due to their toxicity on human, terrestrial and aquatic ecosystems. Toxic levels of metal species in the biosphere are released 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 [1,2].

Heavy 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]. WHO's reports mentioned that lead ions cause nephrotoxicity, hypertension and neurotoxicity. Also, lead removes calcium and therefore it can be found in bones. Elders and children are the most susceptible to lead poisoning [4]. Copper can be accumulated in liver cells and determine hemolytic crisis and neurological disturbances [5].

Due to their extreme toxicity even at low levels, their tendency to accumulate in food chain and their non-biodegradable nature, the heavy metals have to be removed from wastewater before to be discharged into natural waters [6]. Chemical precipitation, ion exchange, sorption, membrane filtration, flotation, reverse osmosis, and electrochemical processes are the main traditional methods used to remediate wastewater and environments polluted with heavy metals [7,8].

Adsorption has been investigated considerably as an economically viable and efficient method to remove heavy metals from wastewater and aqueous solutions. The adsorbents such as activated carbons, fishbone, zeolites, clays, composite materials, starch, chitosan, oxides and hydroxides, fly ash, phosphate, cellulose, carbon nanotubes, biomass-derived sorbents have been extensively used for remediate heavy metals polluted environments [9-11].

One of the most investigated materials in heavy metals removal from wastewaters is hydroxyapatite [10]. Its application in remediation of heavy metals polluted environments is mainly due to physicochemical properties such as large specific area, high thermal and chemical stability and high ionic exchange capacity. Natural and synthetic hydroxyapatite (HAP) can be used for heavy metals removal from wastewaters. Natural hydroxyapatite has as main disadvantage its low purity, and as main advantage its low cost. Many synthetic methods such as synthetic hydroxyapatite chemical precipitation [12], hydrothermal synthesis [13], sol-gel methods [14], multiple cross-linked emulsion techniques [15], biomimetic deposition techniques [16], electrodeposition [17], synthesis in the ultrasonic field [18], microwave assisted synthesis [19, 20] have been involved in the nano- and micrometric HAP particles synthesis. From these methods, the microwave synthesis has as main advantages the reduced synthesis time, and the fact that it is solvent-free being a *greener* synthesis method. Furthermore, it can be used to obtain nanoparticles with controlled shape and particle size. Thus, microwave synthesis is a rather promising method to obtain numerous substances and materials with desired properties.

In our previous researches we obtained nano-hydroxyapatite particles in presence of microwave field from $Ca(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$ as raw materials [19, 20]. The porous HAP granules obtained by microwave assisted synthesis have been employed in the removal of lead and copper removal from single and binary synthetic aqueous solutions [19-21].

The present study focuses on the Pb(II), Ni(II), Zn(II) and Cu(II) removal from polycationic aqueous solutions by nano-HAP particles.

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Experimental part

Materials and testing equipments

Porous HAP granules were obtained according to a method reported in our previous research studies [19, 20]. 1000 mg/L stock Pb(II) solution was prepared by dissolving 1.5986 g of $Pb(NO_3)_2$ (Merck) in 1L distilled water, 1000 mg/L Ni(II) stock solution was prepared by dissolving 4.9547 g $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma-ALdrich) in 1L distilled water, 1000 mg/L ZnII) stock solution was prepared by dissolving 2.8969 g $Zn(NO_3)_2 \cdot 6H_2O$ (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 working solutions were prepared by serial dilution of 1000 mg/L Pb(II), Ni(II), Zn(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 to establish the influence of *p*H to sorption capacity. 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 contact between two phases (solid – HAP and liquid – multicomponent synthetic solutions) was performed by the use of a GFL Shaker 3015 at 150 rpm. Agilent 3200 laboratory pH-meter was used to determine the pH of solutions.

Sorption experiments

The sorption capacity of HAP particles in the removal of Pb(II), Ni(II), Zn(II) and Cu(II) from multicomponent aqueous solutions was tested in batch experiments. Experiments were performed by diluting the stock solutions of Pb(II), Ni(II), Zn(II) and Cu(II) to desired concentrations.

The influence of the contact time on the sorption of Pb(II), Ni(II), Zn((II) and Cu(II) ions was determined from experiments carried out with 0.05 g of HAP and 50 mL of Pb(II), Ni(II), Zn(II)and Cu(II) ions solution at room temperature (21 ± 2°C) at different time (between 1 and 540 min). The initial pH was other parameter investigated. The pH range studied was 2-6. HAP was stirred with the Pb(II), Ni(II), Zn(II) and Cu(II) ions solution at 150 rpm for 600 minutes to reach the equilibrium.

The quantity of Pb(II), Ni(II), Zn(II) and Cu(II) ions adsorbed by HAP particles (mg/g) at equilibrium time, and the removal efficiency (%) were determined by eqs. (1) and (2) below:

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

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

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

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

Results and discussions

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

There is necessary to perform studies related to identify of the pH effect on heavy metal ions adsorption by HAP or other kind of sorbents due to the fact that the most industrial effluents and wastewater with heavy metals content have different *p*H values in function of the type of industrial activities.

Thus, the effect of *p*H on HAP sorption capacity was studied and evaluated by using metal ion solutions adjusted to *p*H 1.5-6.5. The *p*H > 6.5 was excluded due to the possible precipitation of Pb(II), Ni(II), Zn(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), Ni(II), Zn(II) and Cu(II) (mg/g) by HAP in function of *p*H value.

From the figures 1-5, it can be seen that Pb(II), Ni(II), Zn(II) and Cu(II) adsorption on HAP from multicomponent solution is dependent by pH value. Therefore, the next

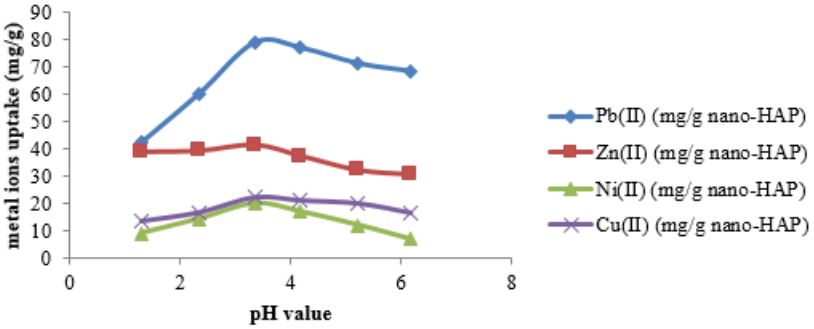

Fig 1. Effect of *p*H on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by HAP from multicomponent solution with 90.72 mg/L Pb(II), 99.39 mg/L Ni(II), 92.32 mg/L Zn(II) and 108.8 mg/L Cu(II)

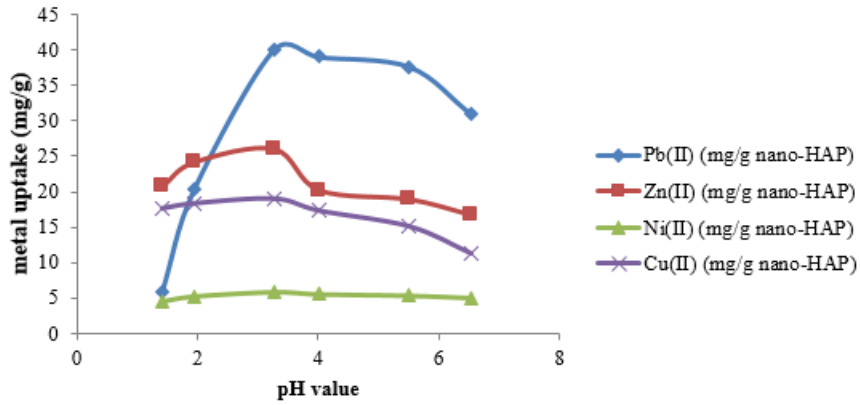

Fig 2. Effect of *p*H on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by HAP from multicomponent solution with 41.1 mg/L Pb(II), 53.09 mg/L Ni(II), 39.15 mg/L Zn(II) and 49.13 mg/L Cu(II)

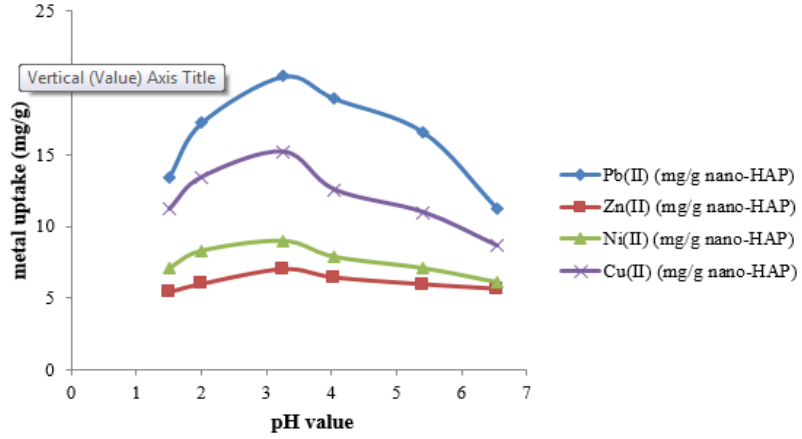

Fig 3. Effect of *p*H on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by HAP from multicomponent solution with 20.87 mg/L Pb(II), 26.82 mg/L Ni(II), 22.44 mg/L Zn(II) and 24.2 mg/L Cu(II)

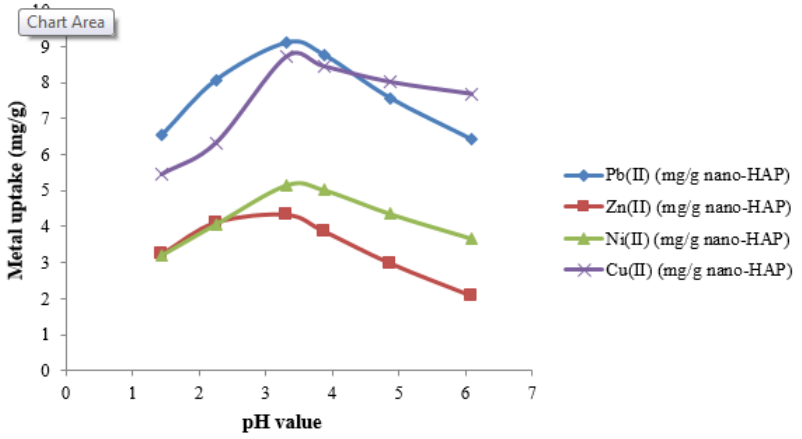

Fig 4. Effect of *p*H on retained amount (mg/g) of Pb(II), Ni)II), Zn(II) and Cu(II) by HAP from multicomponent solution with 9.3 mg/L Pb(II), 13.39 mg/L Ni(II), 11.31 mg/L Zn(II) and 14.28 mg/L Cu(II)

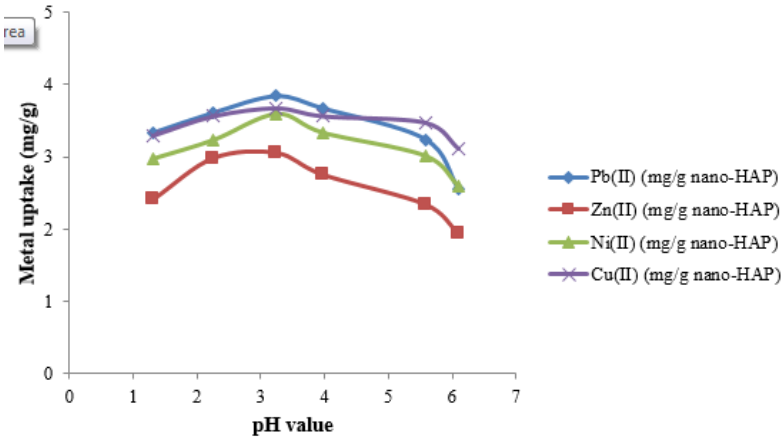

Fig 5. Effect of *p*H on retained amount (mg/g) of Pb(II), Ni)II), Zn(II) and Cu(II) by HAP from multicomponent solution with 4.15 mg/L Pb(II), 5.43 mg/L Ni(II), 5.23 mg/L Zn(II) and 5.05 mg/L Cu(II)

experiments were performed at *p*H solutions value equal with 3.25. This value was reached by adding 0.1M HNO_3.

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

One of the important parameters when dealing with economical evaluation and practical application in water treatment processes is considered the contact time [20]. Therefore, the equilibrium time was determined by batch experiments. The selected shaking time intervals (1, 5, 10, 15, 30, 60, 120, 180, 240, 300, 360, 420, 480, 540 min) were considered to determine the influence of contact time on adsorption capacity and removal efficiency. The results of this study are presented in figures 6-11.

From figures 6-11, it is clear that both the amount of the metal retained by nano-HAP and removal efficiency of the Pb(II), Ni(II), Zn(II) and Cu(II) show a gradual increase with the increasing of the contact time. The maimum values of the amount of heavy metal retained by nano-HAP (defined as sorption capacity) are: 79.02 mg/g for Pb(II), 41.24 mg/g for Zn(II), 21.18 mg/g for Cu(II), and 19.85 mg/g for Zn(II). The maimum values of the removal efficiency are: 87.1 % for Pb(II), 44.66 % for Zn(II), 20.39 % for Cu(II), and 19.97 % for Zn(II). These results lead to the conclusion that nano-HAP synthesised in microwave field has good sorption capacity and selectivity for Pb(II). The following selectivity series was found: Pb(II) > Zn(II) > Cu(II) > Ni(II). From this experimental study, it can be also concluded that the time to reach the equilibrium is 360-420 min. Consequently, Pb(II), Ni(II), Zn(II) and Cu(II) removal by nano-HAP from multicomponent solutions is a fast process.

Adsorption isotherm

The adsorption isotherms are used to describe the relationship between the amount of adsorbed metal ion on the surface of adsorbent and the concentration of metal ion in solution at the equilibrium [21]. Langmuir and Freundlich isotherms are widely used for this purpose. According to Langmuir model, the metal uptake process takes place on the surface of adsorbent in a homogeneous monolayer distribution without any type of interaction

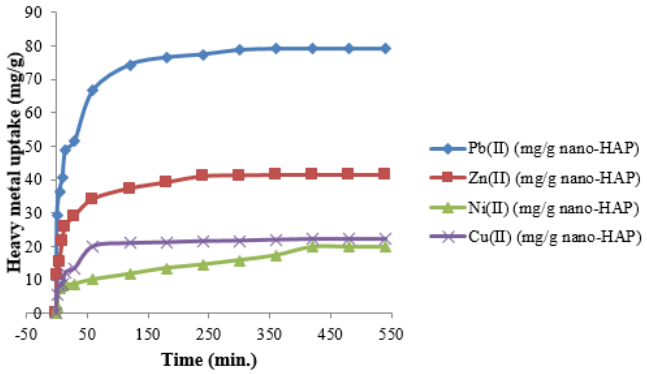

Fig 6. Effect of time on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by HAP from multicomponent solution with 90.72 mg/L Pb(II), 99.39 mg/L Ni(II), 92.32 mg/L Zn(II) and 108.8 mg/L Cu(II)

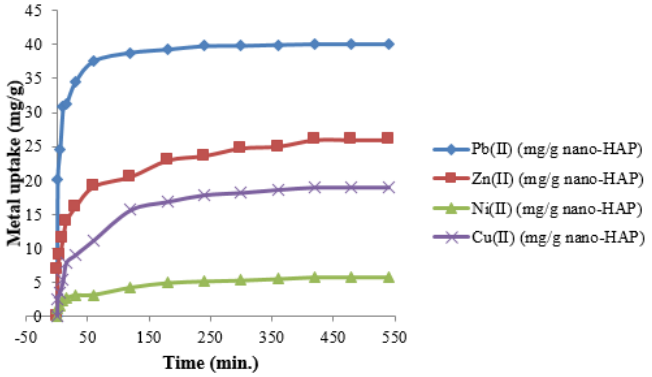

Fig 7. Effect of time on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by HAP from multicomponent solution with 41.1 mg/L Pb(II), 53.09 mg/L Ni(II), 39.15 mg/L Zn(II) and 49.13 mg/L Cu(II)

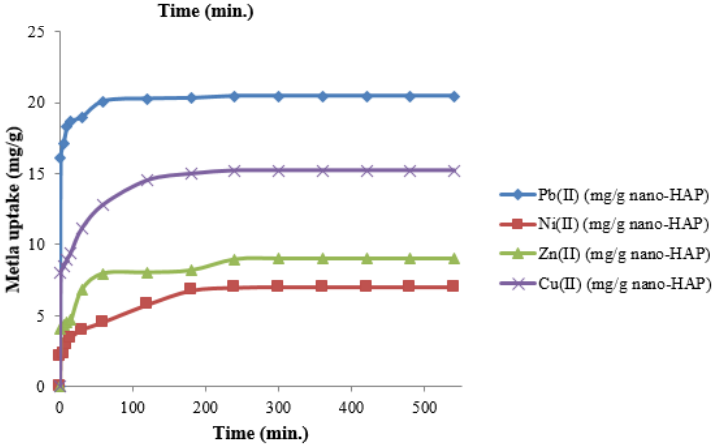

Fig 8. Effect of time on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by HAP from multicomponent solution with 20.87 mg/L Pb(II), 26.82 mg/L Ni(II), 22.44 mg/L Zn(II) and 24.2 mg/L Cu(II)

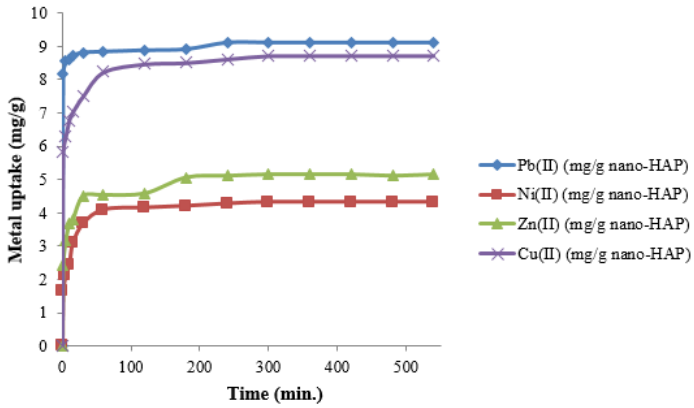

Fig 9. Effect of time on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by HAP from multicomponent solution with 9.3 mg/L Pb(II), 13.39 mg/L Ni(II), 11.31 mg/L Zn(II) and 14.28 mg/ L Cu(II)

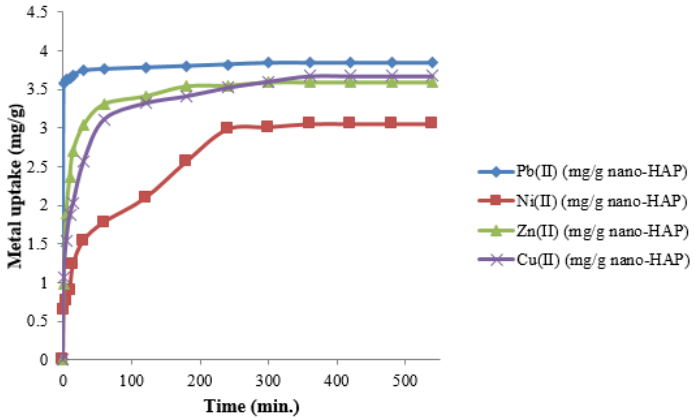

Fig 10. Effect of time on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by HAP from multicomponent solution with 4.15 mg/L Pb(II), 5.43 mg/L Ni(II), 5.23 mg/L Zn(II) and 5.05 mg/L Cu(II)

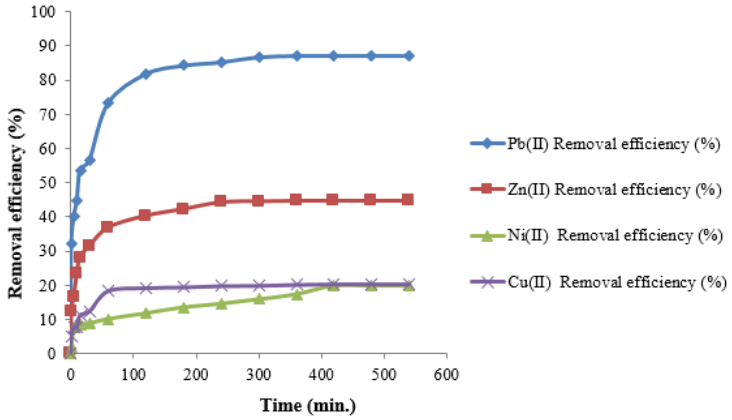

Fig 11. Effect of time on removal efficiency (%) of Pb(II), Ni(II), Zn(II) and Cu(II) by HAP from multicomponent solution with 90.72 mg/L Pb(II), 99.39 mg/L Ni(II), 92.32 mg/L Zn(II) and 108.8 mg/L Cu(II)

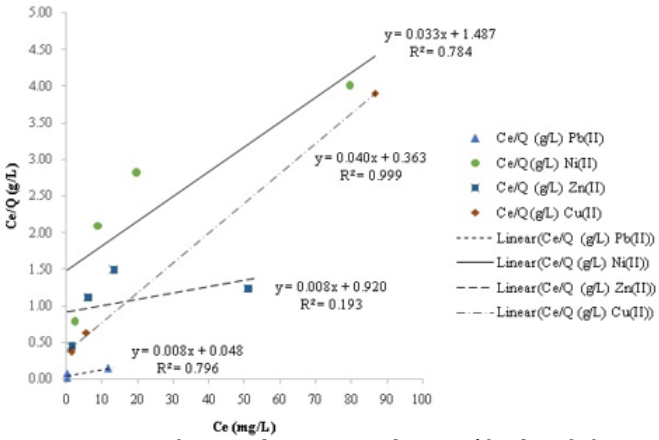

Fig 12. Langmuir linearised sorption isotherms of lead, nickel, zinc and copper from multicomponent systems

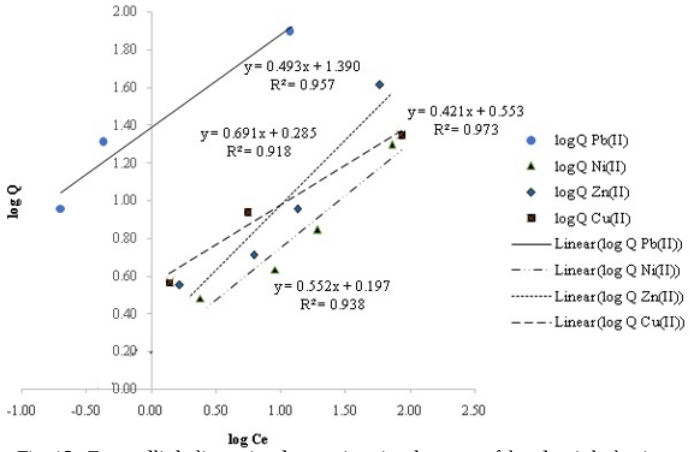

Fig 13. Freundlich linearised sorption isotherms of lead, nickel, zinc and copper from multicomponent systems

Table 1

LANGMUIR AND FEUNDLICH PARAMETERS FOR Pb(II), Ni(II), Zn(II) AND Cu(II) SORPTION BY HAP FROM MULTICOMPONENT 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)	125	6	0.796	24.6	2.0284	0.957
Ni(II)	30.30	45.0561	0.784	1.58	1.8116	0.938
Zn(II)	125	115	0.193	1.93	1.4472	0.918
Cu(II)	25	9.075	0.999	3.57	2.3753	0.973

between adsorbed ions [21]. The adsorption capacities and Langmuir constant can be calculated from Langmuir linearized equation below. (3).

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

where Q_e – the amount of metal ions absorbed per unit mass of adsorbent, C_e - the equilibrium concentration of metal ions (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 [22].

The Freundlich isotherm describes sorption on a heterogeneous surface. This model assumes that the stronger binding sites are occupied first, and then the bonding strengths will decreased with increasing degree of site occupation [23]. The equation for the Freundlich model is eq. (4) [23].

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

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

The logarithm of the equation (4) is:

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

The adsorption linearized isotherms for Pb(II), Ni(II), Zn(II) and Cu(II) sorption on HAP are shown in figures 12 and 13. The Langmuir and Feundlich parameters determined from these plots are introduced in table 1.

By analyzing the figures 12 and 13, and data presented in table 1, it can be say that the Freundlich model adequately described the sorption process for Pb(II), Ni(II) and Zn(II), whereas the Langmuir model described the sorption data for the Cu(II) ions from multicomponent systems. Furthermore, the values of correlation coefficient (R^2) are much closer to the value 1 for Langmuir equation only for Cu(II), they are closer to value 1 for Freudlich model for the others three heavy metal ions. Thus, it can be concluded that Freundlich isotherm could be considered as a better fitting model than Langmuir for Pb(II), Ni(II) and Zn(II), and Langmuir model than Freundlich for Cu(II) sorption on HAP nanoparticles. This indicates the applicability of a monolayer coverage of the Cu(II) ions on the surface of HAP nanoparticles., and sorption of Pb(II), Ni(II) and Zn(II) on the surface of HAP in a homogeneous monolayer distribution without any type of interaction between Pb(II), Ni(II) and Zn(II) adsorbed ions [21].

Adsorption kinetic

The heavy metals sorption onto sorbent materials can be controlled by physical and chemical processes. Thus, it

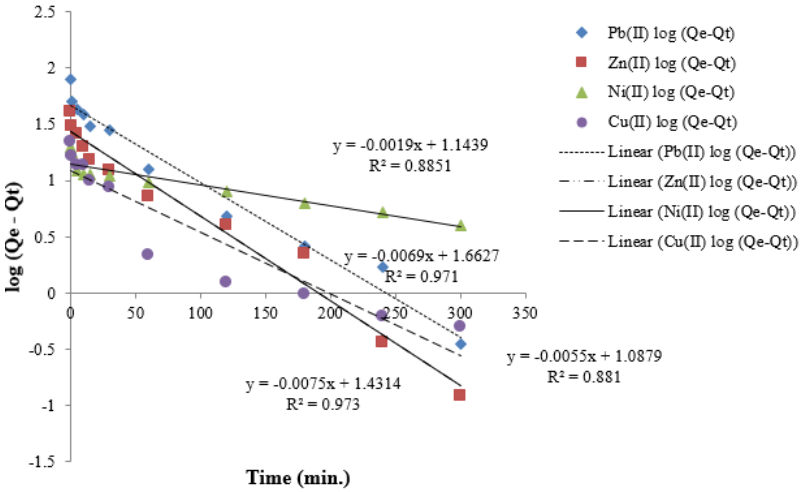

Fig. 14. Pseudo-first order sorption kinetics of Pb(II), Ni(II), Zn(II) and Cu(II) from multicomponent aqueous system onto HAP

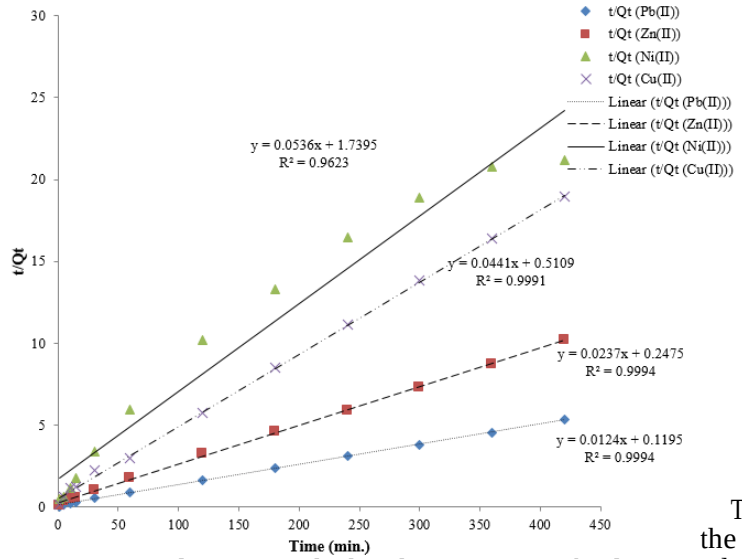

Fig. 15. Pseudo-second order sorption kinetics of Pb(II, Ni(II), Zn(II) and Cu(II) from multicomponent aqueous systems onto HAP

is important to determine which is the process involved in heavy metals sorption. This can be done by determination of adsorption kinetics. The pseudo-first order, pseudo-second order and intraparticle diffusion models have been used to determine the kinetic mechanism of the Pb(II), Ni(II), Zn(II) and Cu(II) from multicomponent systems adsorption process. They also have been used to establish the phases that control the rate of sorption process.

The pseudo-first-order model introduced by Lagergren equation (6) supposes that the rate of adsorption on sorbent is proportional to the number of active sites available onto adsorbent [24].

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

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 equation (7) has been obtained by linearization of the equation (6). This equation (7) has been used to analyze the kinetic data:

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

where Q_e and Q_t represent the amount of Pb(II), Ni(II), Zn(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 pseudo-first order constants (rate constant, k_1 and correlation coefficient, R^2) for Pb(II), Ni(II), Zn(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. 14).

The pseudo-second-order model [25] represented by the equation (8) is determined by the assumption that adsorption follows a chemical sorption (based on chemical reactions):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (8)$$

where: k_2 is the rate constant of second-order adsorption (g/mg·min). The linear plot of t/Qt versus t (fig. 15) has been used to calculate the values of k_2 and Qe and to determine the applicability of the pseudo-second-order kinetic model to the experimental data.

The equation characteristic to the intraparticle diffusion model (9) was also applied to explain the diffusion mechanism [26]:

$$Q_t = k_i t^{0.5} \quad (9)$$

where k_i is intraparticle diffusion rate (mg/g·min). The values of k_i were determined from the slope of straight-line portions of the plot of Q_t against $t^{0.5}$. Intraparticle diffusion kinetic for PbII), Ni(II), Zn(II) and Cu(II) sorption on HAP is presented in figure 16.

Table 2 depicts the sorption constants and the correlation coefficients for all three models used.

Data presented in figure 14-16 and table 3 revealed that pseudo-second-order model is in better agreement with experimental data regarding the kinetics of Pb(II), Ni(II), Zn(II) and Cu(II) ions sorption on HAP prepared with the help of microwave radiation compared to pseudo-first-order and intraparticle diffusion. Thus, in the process of Pb(II), Ni(II), Zn(II) and Cu(II) ions sorption on HAP the rate determining step is chemical adsorption and not physical sorption and the mass transfer.

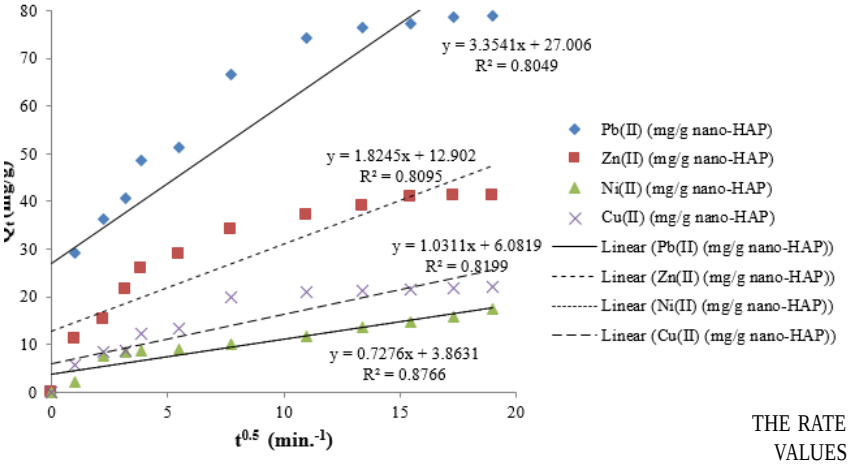

Fig. 16. Intraparticle diffusion sorption kinetics of Pb(II), Ni(II), Zn(II) and Cu(II) onto HAP

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

Heavy metal ions	Pseudo-first order sorption		Pseudo-second order sorption		Intraparticle diffusion	
	k_1 (min^{-1})	R^2	k_2 (g/mg·min)	R^2	k_i (mg/mg·$min^{0.5}$)	R^2
Pb(II)	0.0115	0.971	$1.2101 \cdot 10^{-3}$	0.999	3.354	0.804
Ni(II)	0.0023	0.885	$1.6153 \cdot 10^{-3}$	0.962	0.727	0.876
Zn(II)	0.0161	0.973	$2.1417 \cdot 10^{-3}$	0.999	1.824	0.809
Cu(II)	0.0138	0.881	$3.7961 \cdot 10^{-3}$	0.999	1.031	0.819

Conclusions

An efficient adsorbent for the removal of Pb(II), Ni(II), Zn(II) and Cu(II) ions from multicomponent aqueous solutions was prepared by the use of a rapid microwave method. Optimum removal for all metal ions was obtained at *p*H equal with 3.25 and a contact time of 360-420 min.. Among the adsorption isotherm model tested, the Freundlich model gave the best fit to the experimental data for Pb(II), Ni(II) and Zn(II), whereas the Langmuir model described the sorption data for the Cu(II) ions from multicomponent systems. The kinetic data followed the pseudo-second order kinetic for all four metals chosed. Thus Pb(II), Ni(II), Zn(II) and Cu(II) sorption onto HAP can be described as chemisorptions. The value of sorption capacity recommends HAP as an effective adsorbent of Pb(II), Ni(II), Zn(II) and Cu(II) removal from multi-component aqueous solutions and wastewater. The selectivity of this sorbent follows the series Pb(II) > Zn(II) > Cu(II) > Ni(II).

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