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APPLICABILITY OF CHITOSAN/HYDROXYAPATITE COMPOSITES FOR ADSORPTIVE REMOVAL OF LEAD, COPPER, ZINC AND NICKEL FROM SYNTHETIC AQUEOUS SOLUTIONS

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The purpose of this research paper is to use chitosan/hydroxyapatite composites to remove lead, copper, zinc and nickel from multi-metal aqueous systems. The comparative studies were performed in a batch system. The effects of the removal process parameters such as, pH, contact time, initial metal ions concentration, and type of chitosan/hydroxyapatite composites on the heavy metals removal process were investigated. Freundlich and Langmuir adsorption isotherm models were investigated to determine the adsorption model that better characterize the sorption process. The pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were applied to establish the mechanism involved in sorption process. It was concluded that the properties of hydroxyapatites used as raw materials have an important influence on the sorption properties and selectivity of chitosan/hydroxyapatite composites. These composites can be used as effective adsorbents of heavy metals from aqueous synthetic solutions and wastewater.

Keywords: chitosan/hydroxyapatite composite, heavy metals removal

1. Introduction

Human development and industrialization has a major impact to the environment. Solid, gaseous and liquid wastes have a negative effect to the environment and to human health. Most often these wastes have heavy metals in composition, and consequently they are toxic. Heavy metals such as lead, copper, zinc, cadmium, nickel, arsenic, mercury and chromium are found in industrial

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wastewaters coming from tanneries, pesticides, fertilizers, smelting, metal plating, petroleum, pigments, dyes, mining, textile and glass industries [1-4].

Lead is known to have negative consequences to human health such as: rising of blood pressure, disruption of nervous systems, kidney damage, diminishing learning skills and behavioral disturbances of children [5].

Large quantities of nickel have negative effects such as: developing lung, larynx and prostate cancer, birth anomalies, heart disorders, allergic reactions [5].

High uptakes of copper may produce liver and kidney damage, Wilson's Disease which is characterized by hepatic cirrhosis, demyelization, renal disease, brain damage and copper deposition in the cornea [5].

High levels of zinc have negative consequences such as: stomach cramps, skin irritations, vomiting, nausea, anemia, pancreas damage, arteriosclerosis and disturbance of protein metabolism [5].

Due to these negative effects, there is a need to remove heavy metals from polluted environments. In the case of wastewaters and aqueous solutions loaded with heavy metals, numerous conventional methods were developed to be used for remediation. Among these conventional methods can be mentioned the followings: chemical precipitation, membrane processes, coagulation/flocculation, adsorption, ion exchange, flotation, electrochemical processes, solvent extraction, reverse osmosis. Sorption is one of the most widely used processes due to its flexibility in design, low costs and mild operating conditions. Furthermore, sorption leads to effluents with very low content of heavy metals, and as sorbents can be used a great number of materials. Even waste from different industries such as: food, steel, by-products from combustion [6], agricultural and industrial by-products [7] were used in heavy metals removal from wastewaters.

In recent years, particular interest was granted to develop new and low costs materials with improved sorption capacity and selectivity for heavy metals removal and recovery from wastewater and aqueous solutions.

Chitosan is a biopolymer that has been extensively studied in recent years as an adsorbent due to its low cost, chemical stability and high availability compared to activated carbon [8]. The amino and hydroxyl groups in its structure can serve as active sites for the removal of pollutants from wastewater [8]. Numerous methods were applied to modify chitosan by involving the reactivity of the primary amino groups and the primary and secondary hydroxyl groups [8]. The chemical and physical modified chitosan and its derivatives have shown many advantages over flaked or powdered chitosan [8]. These advantages are due to their higher internal surface area, and beads cross-linking making them insoluble in low pH solutions, thus their using in a broad pH range is easy [8].

The objective of this research study is to bring new contributions to heavy metals removal from aqueous mixed solutions by chitosan/hydroxyapatite composites.

2. Experimental part

Materials and testing equipments

Chitosan/hydroxyapatite composites (CHIT-HAP**)** samples were used as adsorbents for lead, copper, zinc and nickel removal. CHIT-HAP-1 is the sample obtained from chitosan flakes (Fluka origin) and nanohydroxyapatite (HAP) synthesized in presence of microwave field [4]. CHIT-HAP-2 represents the composite obtained from chitosan flakes and HAP synthesized by precipitation of ($Ca(NO_3)_2{\cdot}4H_2O$ and $(NH_4)_2HPO_4$ (all analytical grade, from Merck) followed by calcination at 600°C. In case of the third sample CHIT-HAP-3, HAP used as raw material was prepared by precipitation of ($CaHPO_4{\cdot}4H_2O$, $CaCO_3$ analytical grade, from Merck)) and calcination at 1100°C. The fourth composite sample (CHIT-HAP-4) was prepared from ($Ca(OH)_2$, H_3PO_4) (analytical grade, from Merck) and calcination at 850°C. The chemical and morphological characterization of all four CHIT-HAP samples is presented in our previous paper [9].

Heavy metals stock solutions were prepared as followings: 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 by dissolving 4.9547 g $Ni(NO_3)_2{\cdot}6H_2O$ (Sigma-ALdrich) in 1L distilled water, 1000 mg/L ZnII) stock solution 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 by dissolving 3.8020 g $Cu(NO_3)_2{\cdot}3H_2O$ (Merck) in 1L distilled water.

Batch equilibrium experiments have been carried out by the use of multi-metal solutions obtained by serial dilution of 1000 mg/L Pb(II), Ni(II), Zn(II) and Cu(II) solutions. The influence of pH on sorption capacity of CHIT-HAP composites beads was determined by adjusting the pH of initial solutions with 25% NH_3 solution (NH_4OH), 63% HNO_3 and 0.1M HNO_3 solutions analytical grade, Fluka origin. pH of solutions was set out with the help of Agilent 3200 laboratory pH-meter. Tests were performed in duplicate at room temperature.

Atomic absorption spectrometry was employed to establish the initial metal ions concentration and the remained concentration after the sorption on chitosan/hydroxyapatite composite beads. The ContraAAS®300 Atomic Adsorption Spectrometer was involved for this purpose. All the batch experiments were performed on GFL Shaker 3015 at 150 rpm.

The amount of heavy metals adsorbed on chitosan/hydroxyapatite composite particles (Q), and the removal efficiency (η) have been calculated by the use of the equations (1) and (2):

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

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

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

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

3. Results and discussion

Effect of pH on Pb(II), Ni(II), Zn(II) and Cu(II) removal process by chitosan/hydroxyapatite composite beads

Sorption process is influenced by a series of factors such as: pH value, time, temperature, initial heavy metals concentration and presence of competing ions. The effect of pH is due to the fact that at different pH value, the adsorbent surface has negative or positive charge and the pH value affects the metal ions speciation in aqueous solution. Consequently, repulsive or attraction forces between pollutants and sorbent surface can occur. Moreover, the majority of the industrial effluents and wastewater with heavy metals loading have different pH values depending on the type of industrial activities performed. Thus, it is necessary to carry out studies to establish the influence of the pH value on heavy metal ions adsorption by chitosan/hydroxyapatite beads.

The effect of pH on chitosan/hydroxyapatite composites sorption capacity was researched by using metal ion solutions adjusted to pH 1.7-6.5. Alkaline pH range was not chosen because of the possibility of precipitation of Pb(II), Ni(II), Zn(II) and Cu(II) as hydroxide species.

Figs. 1-4 show the variation of the quantity of Pb(II), Ni(II), Zn(II) and Cu(II) retained by chitosan/hydroxyapatite composites (mg/g) with pH value.

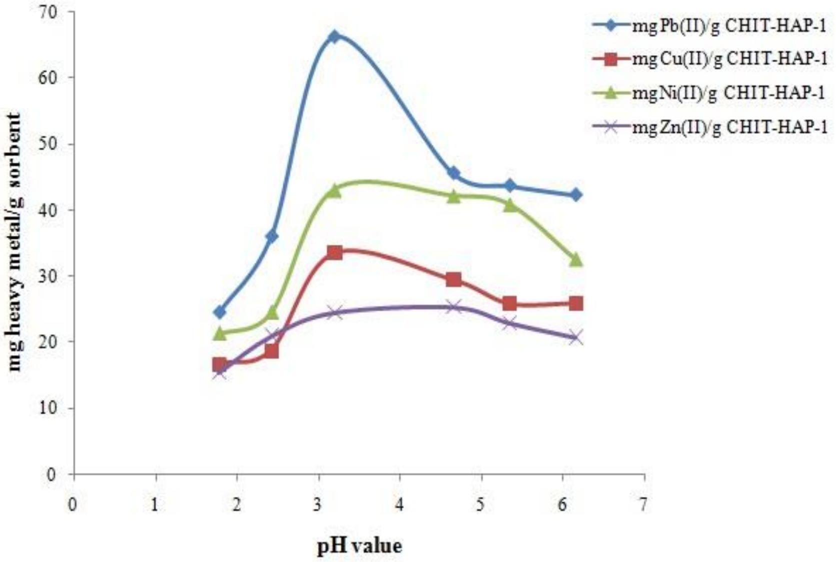

Fig 1. The effect of solution pH on the quantity of heavy metals removed by CHIT-HAP-1

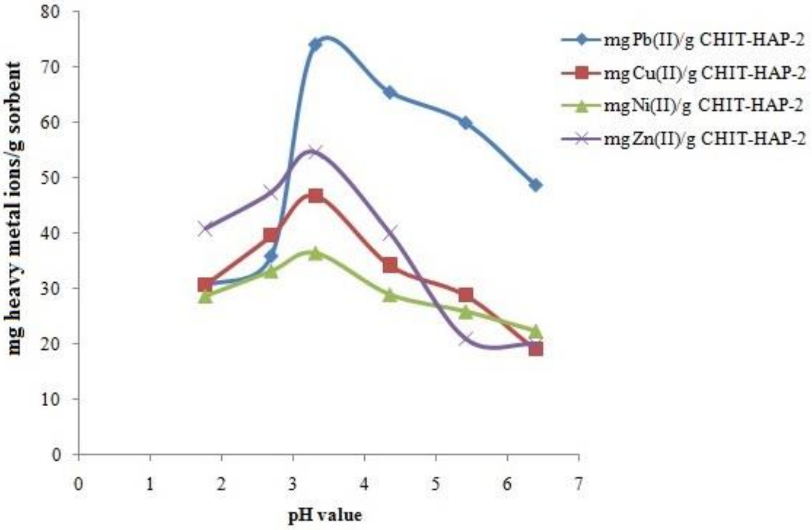

Fig 2. The effect of solution pH on the quantity of heavy metals removed by CHIT-HAP-2

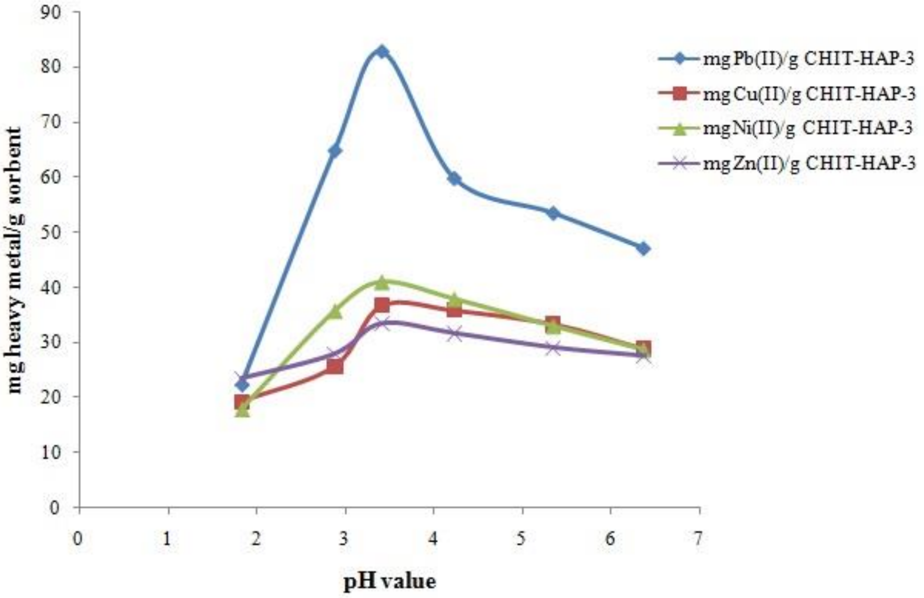

Fig 3. The effect of solution pH on the quantity of heavy metals removed by CHIT-HAP-3

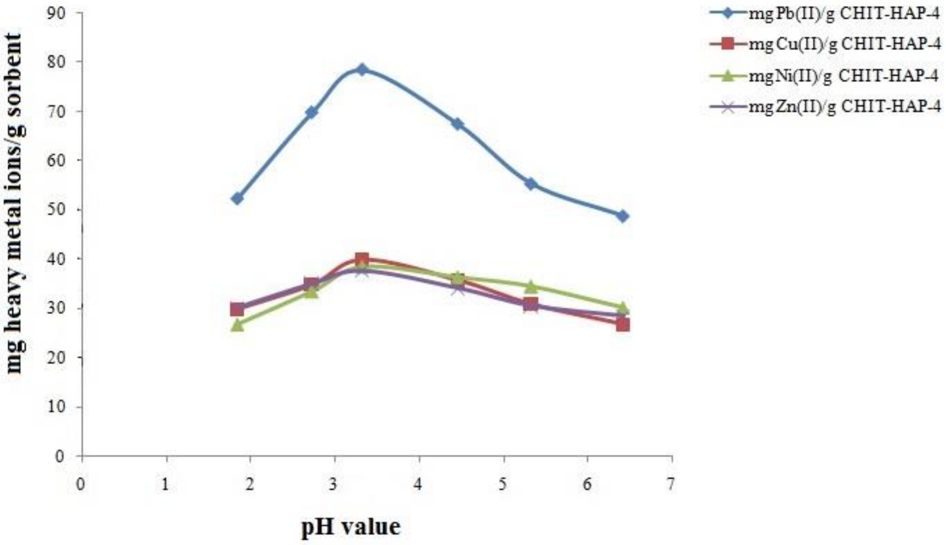

Fig 4. The effect of solution pH on the quantity of heavy metals removed by CHIT-HAP-4

As depicted in Figs. 1-4, the quantity of heavy metal retained by CHIT-HAP composites (mg/g) increases with the increase of pH value until a maximum corresponding to pH value in the interval 3.3 - 3.5 for all four composites. This can be explained by the existing competition between heavy metal ions and H_3O^+ at lower pH values. With the increase of pH value, decrease the concentration of

H_3O^+, and heavy metals can occupy the available sorption sites on the sorbent's surface. After reaching the optimum pH, the heavy metals quantity retained by CHIT-HAP decreases due to the fact that all sorption sites were occupied. This decrease can be due to the fact that at high value of pH a complexation reaction between heavy metal ions and hydroxyl ions from the solution can occurs [10].

It can be also observed that sorption capacity depends on the type of HAP used to prepare the CHIT-HAP composites. The sorption capacity varies in the series Pb(II) > Ni(II) > Cu(II) > Zn(II) for CHIT-HAP-1 and CHIT-HAP-3, and in the series Pb(II) > Zn(II) > Cu(II) > Ni(II) for CHIT-HAP-2 and Pb(II) > Cu(II) > Ni(II) > Zn(II) for CHIT-HAP-4.

Effect of contact time on Pb(II), Ni(II), Zn(II) and Cu(II) removal process by chitosan/hydroxyapatite composite beads

The contact time is one of the most important variables that have to be taken into consideration when designing a heavy metal removal system. Thus, experiments were performed at room temperature, 3.3-3.5 pH and different contact times. The results obtained are presented in Figs. 5-8.

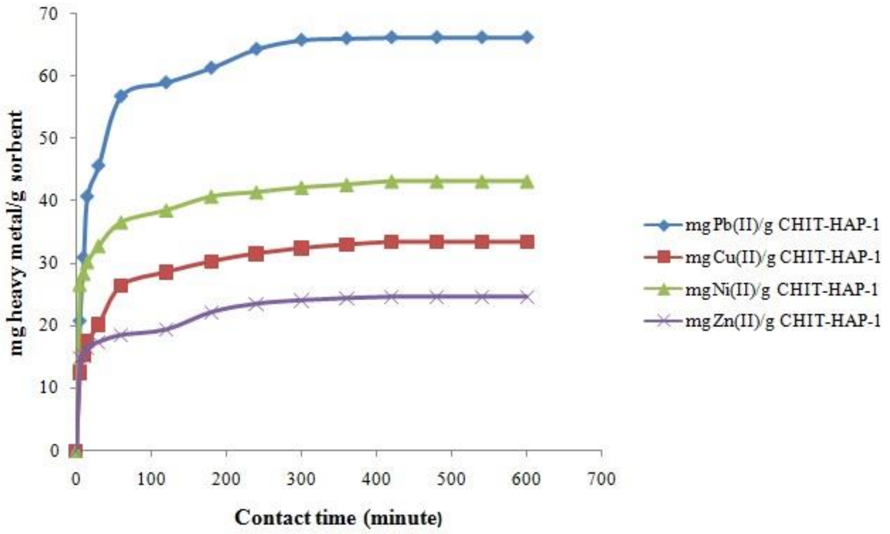

Fig 5. The effect of contact time on the quantity of heavy metals removed by CHIT-HAP-1

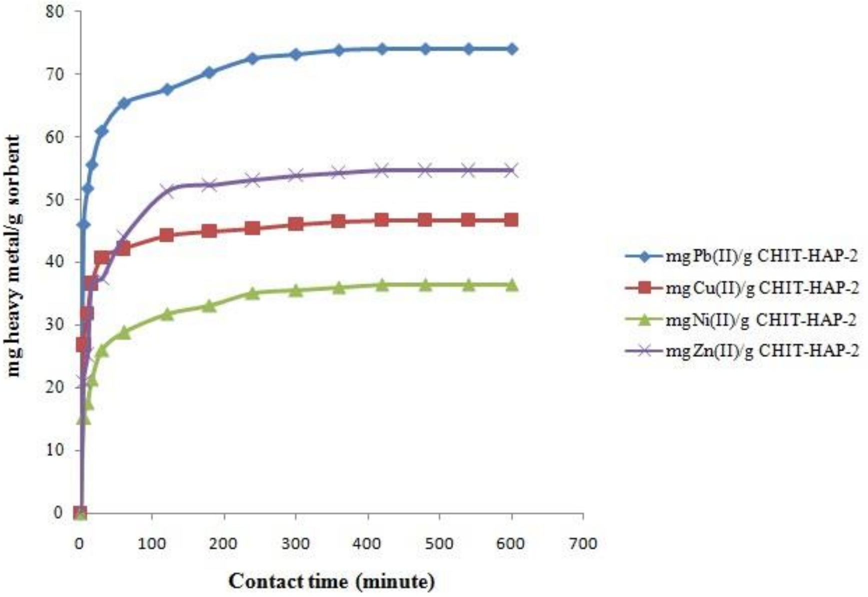

Fig 6. The effect of contact time on the quantity of heavy metals removed by CHIT-HAP-2

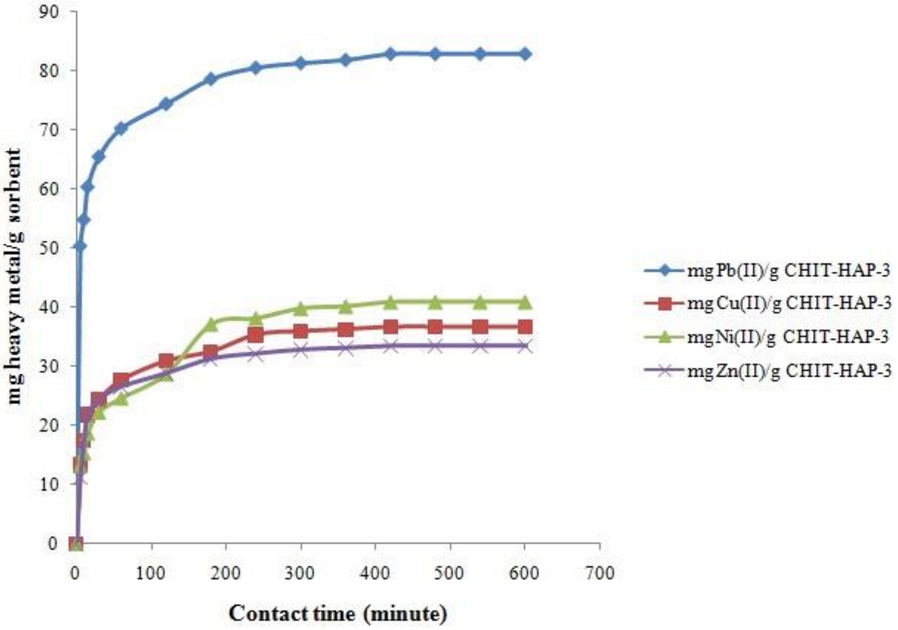

Fig 7. The effect of contact time on the quantity of heavy metals removed by CHIT-HAP-3

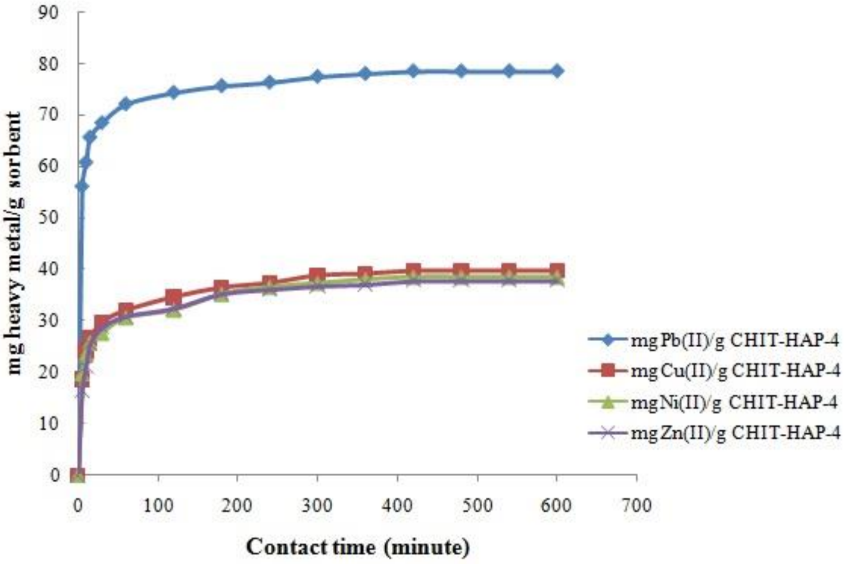

Fig 8. The effect of contact time on the quantity of heavy metals removed by CHIT-HAP-4

The results presented in Figs. 5-8 revealed that for all four materials tested the optimum contact time is 420 minutes and adsorption is fast in the first 60 minutes. After that, a slow increase of adsorption was observed until adsorption equilibrium is reached. In the first fast adsorption stage, all the sorption sites of composites are available and they will be occupied by the heavy metal ions. As the heavy metals adsorption continues more adsorption sites are occupied successively, and consequently the number of free sorption sites will decrease and the adsorption will perform slower. A different behavior of composites in sorption process in function of HAP used for their preparing has been observed.

Adsorption isotherm

The adsorption mechanism is an important issue in designing water/wastewater treatment systems that can be determined by the use of adsorption isotherm. Therefore, establishing the adsorption capacity of sorbent materials with different isotherm models allows to design a treatment process and to optimize operating conditions adequately. Thus, Langmuir and Freundlich adsorption isotherms were adopted to describe the sorption data for Pb(II), Ni(II), Cu(II) and Zn(II) sorption process onto CHIT-HAP composites.

Langmuir model is widely used to describe the sorption process in which metal ions are chemically adsorbed at a fixed number of sorption sites. It is based on the hypothesis that each site will be occupied with only one ion and all sorption sites are energetically equivalent [11].

The equation (3) express the linear form of the Langmuir model:

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

where Q_e is the amount of heavy metal ions retained at equilibrium (mg/g); C_e is the equilibrium concentration of heavy metal ions (mg/L); K_L is the Langmuir model parameter related to energy of adsorption (L/mg) and Q_{max} defines the maximum sorption capacity (mg/g) [11].

Freundlich model assumes that the concentration of adsorbate on the adsorbent surface increases with the adsorbates concentration and an infinite amount of adsorption can take place [11]. This model is generally used to describe a sorption process on heterogeneous surfaces.

The equation (4) depicts the Freundlich model:

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

where K_F is Freundlich constant which represents sorption capacity and n is Freundlich constant that show sorption intensity [10].

The linear form of Freundlich model is shown in Equation (5):

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

The tests were performed with multi-metal solutions to find sorption isotherm that describes the heavy metals sorption onto CHIT-HAP composites.

The Figures below present the linear forms of equilibrium isotherms. They have been used to determine values of sorption parameters.

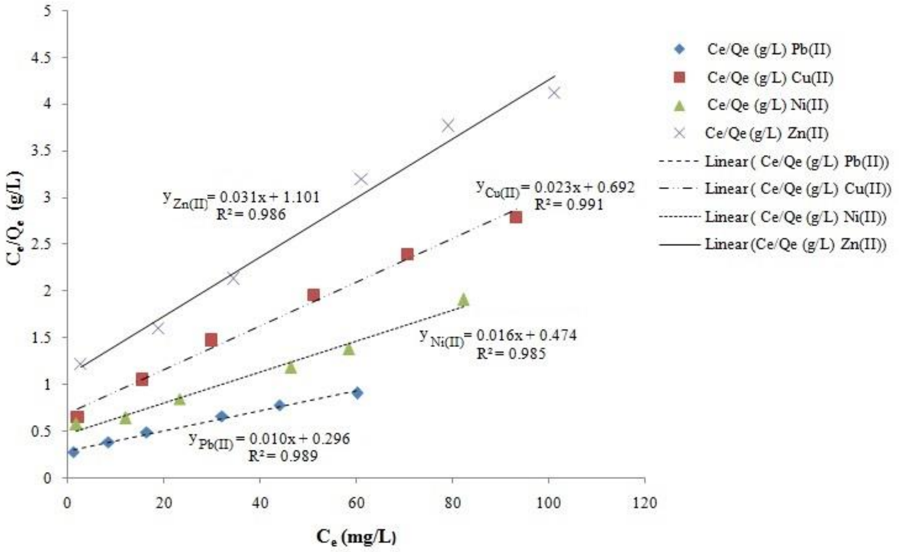

Fig. 9. Langmuir linearized isotherm for Pb(II), Cu(II), Ni(II) and Zn(II) sorption onto CHIT-HAP-1 composite

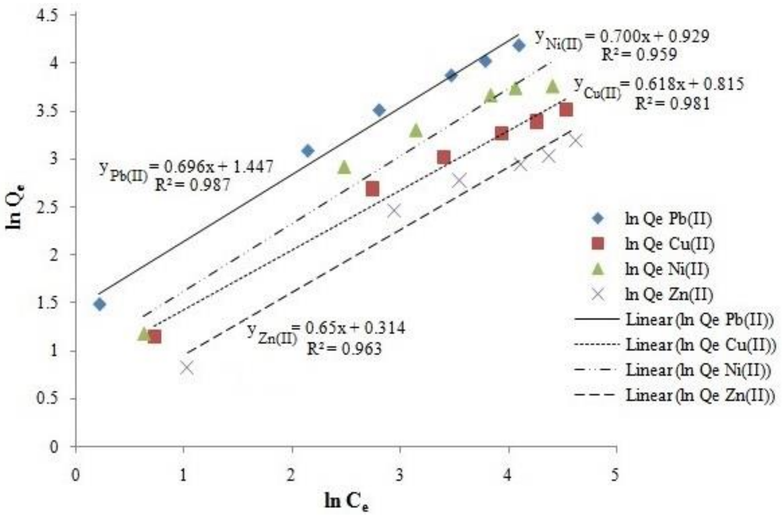

Fig. 10. Freundlich linearized isotherm for Pb(II), Cu(II), Ni(II) and Zn(II) sorption onto CHIT-HAP-1 composite

The Langmuir and Feundlich parameters determined from these plots are presented in Table 1 for all four composites tested.

Table 1

Langmuir and Freundlich parameters for Pb(II), Cu(II), Ni(II) and Zn(II) sorption onto CHIT-HAP composites

CHIT-HAP-1/Metal ion	**Langmuir parameters**			**Freundlich parameters**		
	Q_{max} (mg/g	**K_L (L/mg)**	**R^2**	**K_F (mg/g)**	**n**	**R^2**
Pb(II)	100	0.0338	0.989	4.25	1.4368	0.987
Ni(II)	32.26	0.0282	0.985	2.53	1.4286	0.959
Zn(II)	62.5	0.0338	0.986	1.37	1.5385	0.963
Cu(II)	43.48	0.0332	0.991	2.26	1.6181	0.981
CHIT-HAP-2/Metal ion	**Q_{max} (mg/g**	**K_L(L/mg)**	**R^2**	**K_F (mg/g)**	**n**	**R^2**
Pb(II)	14.29	0.2194	0.996	3.66	1.2723	0.991
Ni(II)	43.48	0.0459	0.989	2.95	1.7153	0.969
Zn(II)	71.43	0.0458	0.986	4.37	1.6207	0.989
Cu(II)	71.43	0.0258	0.997	2.45	1.4104	0.985
CHIT-HAP-3/Metal ion	**Q_{max} (mg/g**	**K_L(L/mg)**	**R^2**	**K_F (mg/g)**	**n**	**R^2**
Pb(II)	111.11	0.0634	0.989	7.71	1.5060	0.984
Ni(II)	50	0.0491	0.988	3.68	1.7699	0.985
Zn(II)	41.67	0.0489	0.992	3.03	1.7637	0.980
Cu(II)	45.45	0.0441	0.995	2.85	1.6611	0.970
CHIT-HAP-4/Metal ion	**Q_{max} (mg/g**	**K_L(L/mg)**	**R^2**	**K_F (mg/g)**	**n**	**R^2**
Pb(II)	125	0.0365	0.997	5.07	1.3298	0.984
Ni(II)	47.62	0.0426	0.988	3.39	1.7036	0.981
Zn(II)	52.63	0.0259	0.990	1.97	1.4684	0.985
Cu(II)	55.56	0.0271	0.991	2.13	1.4684	0.980

Experimental data presented in Figs. 9 and 10, and Table 1 revealed that Langmuir isotherm model fits the experimental data ($R_L^2 > R_F^2$) for all four CHIT-HAP composite samples tested. Thus, it can be concluded that the monolayer adsorption isotherm is more suitable to explain the adsorption of Pb(II), Ni(II). Zn(II) and Cu(II) onto CHIT-HAP composites.

Adsorption kinetics

A kinetic study is fundamental to determine the mechanism involved in pollutants sorption. Thus, a kinetic study was performed to quantify the adsorption rate controlling steps in heavy metals uptake from multi-metal systems on CHIT-HAP composites samples. The pseudo-first-order, the pseudo-second-order and intraparticle diffusion kinetic models were used for this purpose [12].

Pseudo-first-order model was first introduced by Lagergren (equation (6). It assumes that the rate of adsorption on sorbent is proportional to the number of active sites available onto adsorbent [12].

$$\frac{dQ_t}{dt} = k_1\left(Q_e - Q_t\right) \tag{6}$$

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 pseudo-first-order kinetic model equation is represented by equation (7) being used to analyze the kinetic data:

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

where Q_e and Q_t represent the amount of Pb(II), Ni(II), Zn(II) and Cu(II) adsorbed onto CHIT-HAP composites (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 for Pb(II), Ni(II), Zn(II) and Cu(II) sorption onto CHIT-HAP composites have been determined from the slope and the intercept of the liner plot of $\log(Q_e\text{-}Q_t)$ versus t (Fig. 11).

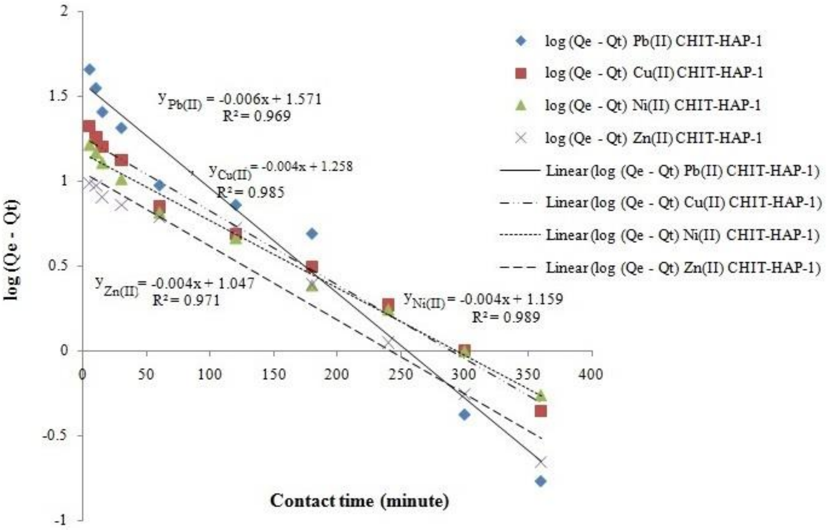

Fig 11. Pseudo-first order sorption kinetics of Pb(II), Ni(II), Zn(II) and Cu(II) from multi-metal aqueous system onto CHIT-HAP-1 composite

The pseudo-second-order (expressed by the equation (8)) is based on the assumption that adsorption follows the mathematical relation [13]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{8}$$

where: k_2 is the rate constant of second-order adsorption (g/mg·min). The values of k_2 and Qe have been calculated from the linear plot of t/Qt versus t (Fig. 12).

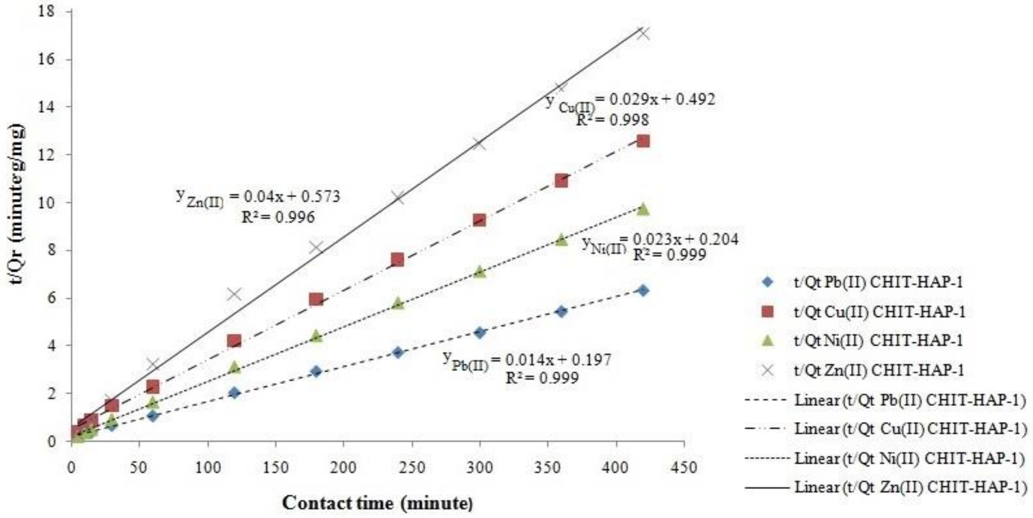

Fig. 12. Pseudo-second order sorption kinetics of Pb(II, Ni(II), Zn(II) and Cu(II) from multi-metal aqueous systems onto CHIT-HAP-1 composite

The diffusion mechanism is determined by the use of intraparticle diffusion model of Weber and Morris (9) [14]:

$$Q_t = k_i t^{0.5} + c \tag{9}$$

where k_i is intraparticle diffusion rate (mg/g·min), and c is intercept (calculated from the slope of straight-line portions of the plot of Q_t against $t^{0.5}$ (Fig 13).

The rate limiting step is the intra-particle diffusion in the situation when the plot of Pb(II), Ni(II), Zn(II) and Cu(II) sorption onto CHIT-HAP composites yields a straight line passing through the origin [14].

From Fig. 13 it can be seen that the curves for all four heavy metals could be divided in two stages. A linear part at the beginning followed by a non-linear part can be observed. This shape of curves indicates that more than one process was involved in the adsorption of heavy metal ions onto CHIT-HAP-1 composite.

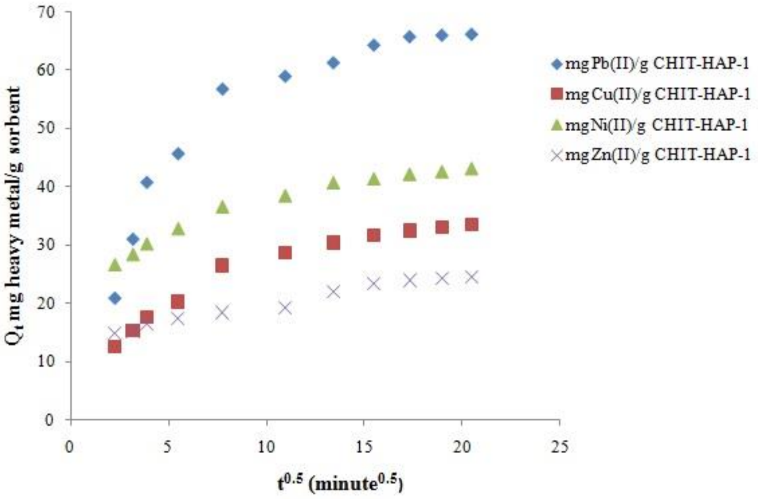

Fig. 13. Intraparticle diffusion sorption kinetics of Pb(II), Ni(II), Zn(II) and Cu(II) onto CHIT-HAP-1 composite

The values of sorption constants and R^2 for pseudo-first-order and pseudo-second-order kinetic models have been calculated being summarized in Table 2.

Table 2

The rate constant and correlation coefficient (R^2) values for Pb(II), Cu(II), Ni(II) and Zn(II) sorption onto CHIT-HAP-1 composite

Heavy metal ions	Pseudo-first order sorption		Pseudo-second order sorption	
	k_1 (min^{-1})	R^2	k_2 (g/mg·min)	R^2
Pb(II)	$1.3818 \cdot 10^{-2}$	0.969	$9.9492 \cdot 10^{-4}$	0.999
Ni(II)	$9.212 \cdot 10^{-3}$	0.989	$2.5931 \cdot 10^{-3}$	0.999
Zn(II)	$9.212 \cdot 10^{-3}$	0.971	$2.7923 \cdot 10^{-3}$	0.996
Cu(II)	$9.212 \cdot 10^{-3}$	0.985	$1.7093 \cdot 10^{-3}$	0.998

The data presented in Figs. 11-13 and Table 2 revealed that the pseudo-second-order kinetic model is in better agreement with experimental data regarding the kinetics of Pb(II), Ni(II), Cu(II) and Zn(II) ions sorption on CHIT-HAP-1 composite compared to pseudo-first-order and intraparticle difussion kinetic models. Similar results have been obtained for the other CHIT-HAP-composites tested. According to this kinetic model the rate determining step is chemical adsorption and not physical sorption or the mass transfer [14].

6. Conclusions

Pb(II), Ni(II), Cu(II) and Zn(II) ions sorption on different CHIT-HAP composites were studied in the present work. The results obtained showed that the type of HAP sample used to prepare CHIT-HAP composites has an important influence on the sorption properties of CHIT-HAP composites. Adsorption of

Pb(II), Ni(II), Cu(II) and Zn(II) onto CHIT-HAP composites was found to be effective in the pH range 3.2-3.4. The Langmuir isotherm equation was found to best represent the experimental adsorption data obtained from the adsorption of Pb(II), Ni(II), Cu(II) and Zn(II) onto CHIT-HAP composites from multi-metal aqueous solutions. The adsorption kinetics followed the mechanism of the pseudo-second-order equation for all four metal ions sorbed by CHIT-HAP composites. This confirms that the chemical adsorption is the rate-limiting step. The selectivity and sorption properties of CHIT-HAP composites depend on the raw materials used for their synthesis.

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