

Removal of Lead(II), Nickel(II), Zinc(II) and Copper(II) from Multi-metal Systems by Chitosan-glutaraldehyde Beads

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The aim of this work was to use glutaraldehyde-crosslinked chitosan (Chit-GLA) beads to remove lead(II), nickel(II), zinc(II) and copper(II) from polycationic aqueous solutions. The batch experiments were carried on to test the influence of different parameters such as: pH, contact time, and initial ion concentration on adsorption of metal ions onto glutaraldehyde-crosslinked chitosan beads. The results obtained revealed that removal ration decreased in the order: 74.06 for Pb(II), 73.45 for Ni(II), 73.16 for Zn(II), and 72.77% for Cu(II) in mixed solutions with the initial solution with concentration 90.72 mg Pb(II)/L, 99.39 mg Ni(II)/L, 92.32 mg Zn(II)/L, and 108.8 mg Cu(II)/L. The maximum adsorption capacity of 67.19 mg Pb(II)/g Chit-GLA, 67.81 mg Ni(II)/g Chit-GLA, 72.71 mg Zn(II)/g Chit-GLA and 79.18 mg Cu(II)/g Chit-GLA were achieved. The results of this research study can lead to the conclusion that glutaraldehyde-crosslinked chitosan beads can be used for the removal of lead, nickel, zinc and copper from polycationic aqueous solutions and wastewater. The series: Cu(II) > Zn(II) > Ni(II) > Pb(II) was proposed as the selectivity series of Chit-GLA beads.

Keywords: lead, nickel, zinc and copper removal, glutaraldehyde-crosslinked chitosan beads

The growing rate of development of civilization has a big contribution to pollution of the environment. One of the most concerns is heavy metals pollution due to the fact that heavy metals have negative effects to humans, plants and animals. It is well known that tannery, fertilizers industry, textile industries, metal plating, mining industries, batteries production, pigment and dyes industries, glass industry, electrochemical processes, pesticides and wood preservatives production are the main anthropogenic sources of heavy metals [1].

Many reports regarding the effects of heavy metals on human health have been developed by international organizations such as the World Health Organization (WHO) [2]. Among the heavy metals with high levels of toxicity, lead ions are known to cause nephrotoxicity, hypertension and neurotoxicity. Another negative effect of lead is that it removes calcium ions and therefore it can be found in bones. Lead poisoning is more significant for elders and children [3]. In human body, copper can be accumulated in liver cells and it determines hemolytic crisis and neurological disturbances [4]. Zinc can cause gastrointestinal disorders and convulsions [5]. It was also suggested that nickel plays a role in breast cancer [5].

Heavy metals characteristics such as their extreme toxicity even at low levels, their tendency to accumulate in food chain and their non-biodegradable nature imposed law restrictions regarding water pollution. Thus, the heavy metals have to be removed from wastewater before to be discharged into natural waters [6]. Several treatment techniques are used for this purpose, such as chemical precipitation, ion exchange, sorption, membrane filtration, flotation, reverse osmosis, and electrochemical processes [7, 8]. Among these, adsorption has been investigated considerably as an economically viable and efficient method to remediate aquatic environments polluted with heavy metals. For this purpose, 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 applied [9-11].

Among efficient synthetic sorbents used in wastewater treatment, special attention is paid to chitosan due to its metal ions chelating capacity [1], relative availability, biodegradability and amenability to chemical modification [12]. Chitosan has semi-crystalline nature and relatively low surface area. Consequently, it is generally a poor adsorbent in its unmodified form. Furthermore, it has good solubility in acidic media being difficult to be removed after pollutants sorption processes.

Many studies were performed to use of cross-linkers to modify chemical structure of chitosan and its textural properties. Usually this process involves linking at the amine or the hydroxyl sites of chitosan [12, 13]. A porous material with improved sorption properties and high stability in acidic media can be obtained by cross-linking of glutaraldehyde to chitosan. Furthermore, it can be obtained copolymers with different morphology such as beads, hydrogels, powders, membranes and films [12].

The present study focuses on the Pb(II), Ni(II), Zn(II) and Cu(II) removal from polycationic aqueous solutions by glutaraldehyde-crosslinked chitosan beads which were previously obtained and characterized [14].

Experimental part

Materials and testing equipments

Glutaraldehyde-crosslinked chitosan beads (Chit-GLA) were obtained according to a method reported in our previous research studies [14]. In this research study, Chit-GLA 0.1% beads were tested due to the fact that they have higher sorption capacity. They were obtained by the use of a solution of 0.1% glutaraldehyde. Stock solutions were prepared as followings: 1000 mg/L stock Pb(II) solution was prepared by dissolving 1.5986 g of $\text{Pb}(\text{NO}_3)_2$ (Merck) in 1L distilled water, 1000 mg/L Ni(II) stock solution by dissolving 4.9547 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-ALdrich) in 1L distilled water, 1000 mg/L Zn(II) stock solution by dissolving 2.8969 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck) in 1L distilled water and 1000 mg/L Cu(II) stock solution by dissolving 3.8020 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merck) in 1L distilled water. In batch experiments were used multi-metal solutions obtained by

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serial dilution of 1000 mg/L Pb(II), Ni(II), Zn(II) and Cu(II) solutions. To test the influence of pH to sorption capacity of glutaraldehyde-crosslinked chitosan beads, the pH of initial solutions was adjusted by the use of 25% NH₃ solution (NH₄OH), 63% HNO₃ and 0.1M HNO₃ solutions analytical grade, Fluka origin. Agilent 3200 laboratory pH-meter was used to determine the pH of solutions.

Atomic absorption spectrometry was applied to determine the initial metal ions concentration and the remained concentration after the sorption on glutaraldehyde-crosslinked chitosan beads. For this purpose, ContraAAS[®] 300 Atomic Adsorption Spectrometer was used. All the experiments were carried out on GFL Shaker 3015 at 150 rpm.

Sorption experiments

The sorption capacity of glutaraldehyde-crosslinked chitosan beads in the removal of Pb(II), Ni(II), Zn(II) and Cu(II) from multi-metal aqueous solutions was determined in batch experiments. Multi-metal solutions were prepared by diluting the stock solutions of Pb(II), Ni(II), Zn(II) and Cu(II) to desired concentrations.

The studies relating to the effect of the contact time on the sorption of Pb(II), Ni(II), Zn(II) and Cu(II) ions were performed by the use of 0.05 g of glutaraldehyde-crosslinked chitosan beads 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 minutes).

The effect of pH on heavy metals adsorption capacity and removal efficiency was studied in pH range 1.5 - 6.5. Glutaraldehyde-crosslinked chitosan beads were stirred with the Pb(II), Ni(II), Zn(II) and Cu(II) ions solution at 150 rpm for 480 min to reach the equilibrium.

The mass of Pb(II), Ni(II), Zn(II) and Cu(II) ions adsorbed by glutaraldehyde-crosslinked chitosan beads (mg/g) at equilibrium time, and the removal efficiency (%) were determined as follows:

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

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 glutaraldehyde-crosslinked chitosan beads 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 glutaraldehyde-crosslinked chitosan beads

pH is one of the important parameters with influence on sorption process due to the fact that at different pH value, the adsorbent surface has negative or positive charge and thus can occur repulsive or attraction forces between pollutants and adsorbent surface. Furthermore, the pH value influences the metal ions speciation in aqueous solution and the most industrial effluents and wastewater with heavy metals content have different pH values in function of the type of industrial activities. Thus, it is necessary to perform studies related to the influence of pH value on heavy metal ions adsorption by glutaraldehyde-crosslinked chitosan beads.

The effect of pH on glutaraldehyde-crosslinked chitosan beads sorption capacity was studied by using metal ion solutions adjusted to pH 1.5-6.5. Alkaline conditions were not tested because of the probability of precipitation of Pb(II), Ni(II), Zn(II) and Cu(II) as hydroxide species.

Figures 1-5 depict the variation of the quantity of Pb(II), Ni(II), Zn(II) and Cu(II) retained by glutaraldehyde-crosslinked chitosan (mg/g) with pH value.

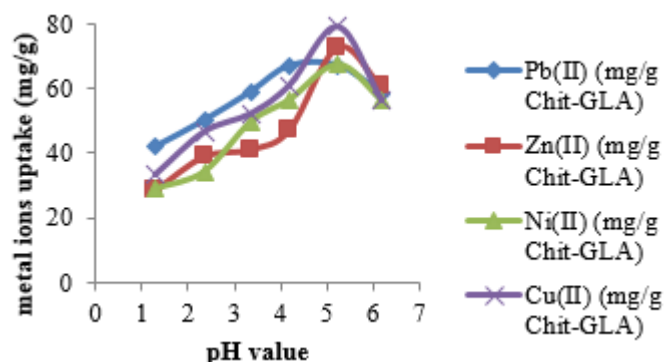


Fig 1. Effect of pH on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by glutaraldehyde-crosslinked chitosan from multi-metal solution with 90.72 mg/L Pb(II), 99.39 mg/L Ni(II), 92.32 mg/L Zn(II) and 108.8 mg/L Cu(II)

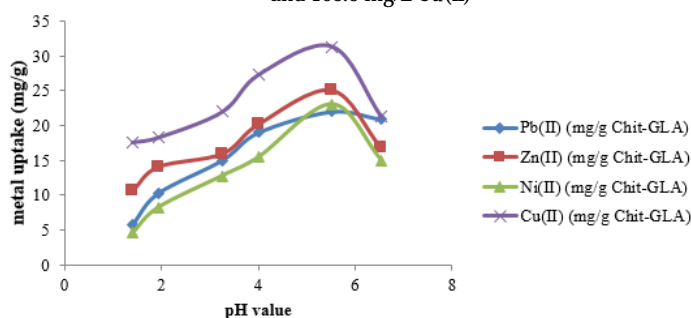


Fig 2. Effect of pH on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by glutaraldehyde-crosslinked chitosan from multi-metal solution with 41.1 mg/L Pb(II), 53.09 mg/L Ni(II), 39.15 mg/L Zn(II) and 49.13 mg/L Cu(II)

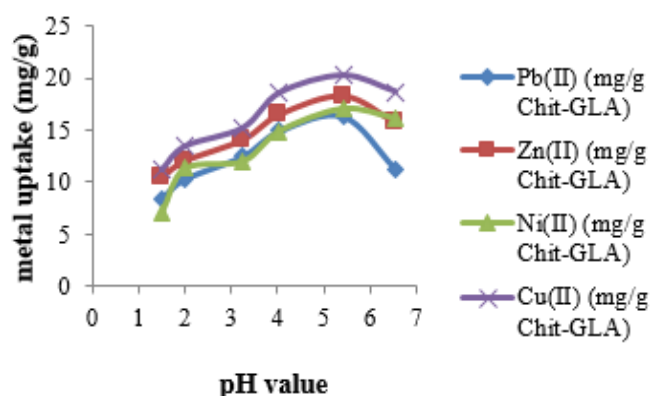


Fig 3. Effect of pH on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by glutaraldehyde-crosslinked chitosan from multi-metal solution with 20.87 mg/L Pb(II), 26.82 mg/L Ni(II), 22.44 mg/L Zn(II) and 24.2 mg/L Cu(II)

The results presented in figures 1-5 showed that increasing the initial pH enhanced the quantity of heavy metals retained by Chit-GLA beads till an optimum pH value for all the heavy metals tested. After this value, it can be observed a decreasing of quantity of heavy metals retained by Chit-GLA beads. The value for optimum pH is the value of heavy metals solutions pH value, and therefore the next experiments were performed at pH solutions without any adjustments.

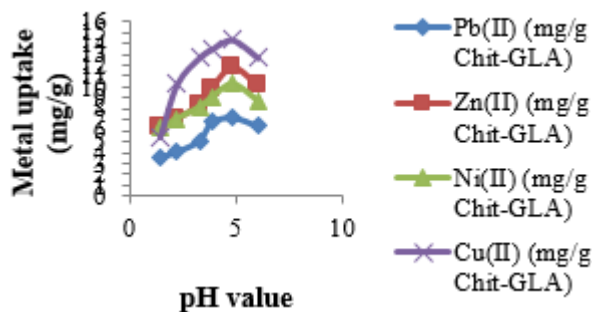


Fig 4. Effect of pH on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by glutaraldehyde-crosslinked chitosan from multi-metal solution with 9.3 mg/L Pb(II), 13.39 mg/L Ni(II), 11.31 mg/L Zn(II) and 14.58 mg/L Cu(II)

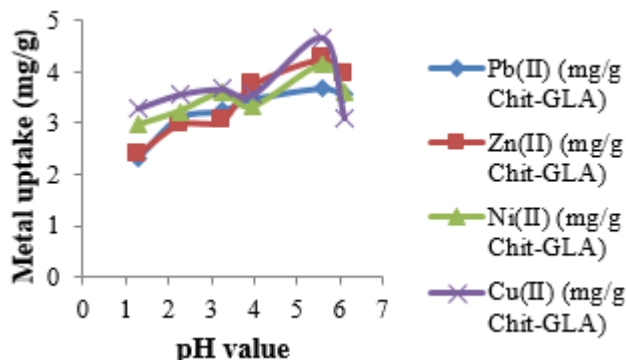


Fig 5. Effect of pH on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by glutaraldehyde-crosslinked chitosan from multi-metal solution with 4.15 mg/L Pb(II), 5.43 mg/L Ni(II), 5.23 mg/L Zn(II) and 5.05 mg/L Cu(II)

Effect of time on Pb(II), Ni(II), Zn(II) and Cu(II) removal process by Chit-GLA beads

The equilibrium time is one of the most important parameters for designing the wastewater treatment system at industrial scale [15]. The batch experiments were performed at different shaking time intervals (1, 5, 10, 15, 30, 60, 120, 180, 240, 300, 360, 420, 480, 540 min) to determine the equilibrium time. The effect of contact time on adsorption capacity and removal efficiency is presented in figures 6-11.

Figures 6-11 revealed that both the amount of the metal retained by Chit-GLA and removal efficiency of the Pb(II), Ni(II), Zn(II) and Cu(II) increase rapidly at the first 60 min. After this time, the quantity of metal retained by Chit-GLA and removal efficiency will increase slowly. The maximum values of the amount of heavy metal retained by Chit-GLA are: 67.19 mg/g for Pb(II), 72.71 mg/g for Zn(II), 67.81 mg/g for Ni(II), and 79.18 mg/g for Cu(II). The maximum values of the removal efficiency are: 74.06 % for Pb(II),

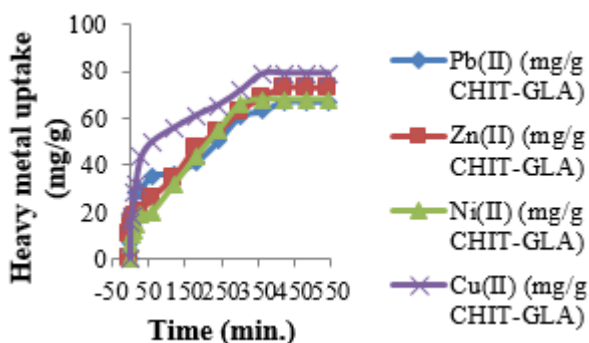


Fig 6. Effect of time on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by glutaraldehyde-crosslinked chitosan from multi-metal solution with 90.72 mg/L Pb(II), 99.39 mg/L Ni(II), 92.32 mg/L Zn(II) and 108.8 mg/L Cu(II)

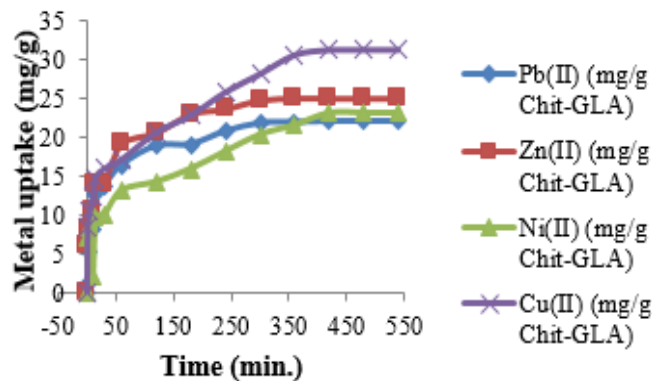


Fig 7. Effect of time on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by glutaraldehyde-crosslinked chitosan from multi-metal solution with 41.1 mg/L Pb(II), 53.09 mg/L Ni(II), 39.15 mg/L Zn(II) and 49.13 mg/L Cu(II)

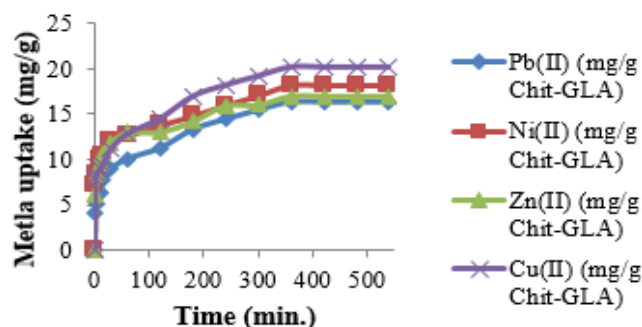


Fig 8. Effect of time on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by glutaraldehyde-crosslinked chitosan from multi-metal solution with 20.87 mg/L Pb(II), 26.82 mg/L Ni(II), 22.44 mg/L Zn(II) and 24.2 mg/L Cu(II)

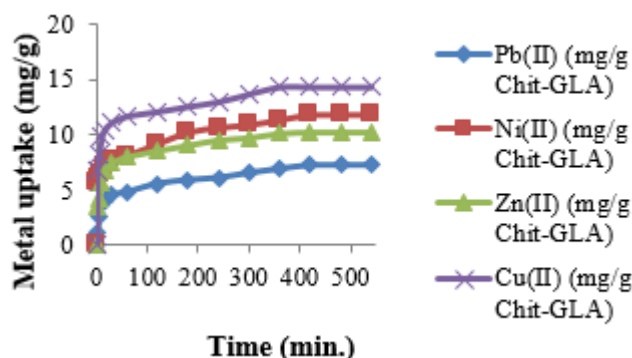


Fig 9. Effect of time on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by glutaraldehyde-crosslinked chitosan from multi-metal solution with 9.3 mg/L Pb(II), 13.39 mg/L Ni(II), 11.31 mg/L Zn(II) and 14.58 mg/L Cu(II)

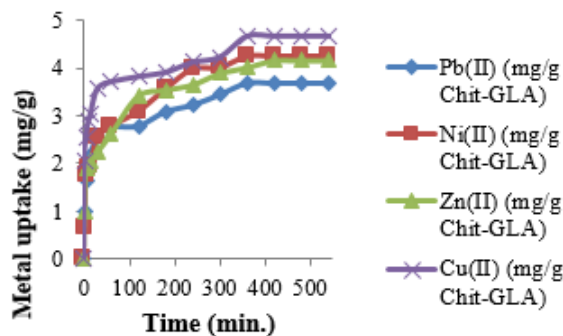


Fig 10. Effect of time on retained amount (mg/g) of Pb(II), Ni(II), Zn(II) and Cu(II) by glutaraldehyde-crosslinked chitosan from multi-metal solution with 4.15 mg/L Pb(II), 5.43 mg/L Ni(II), 5.23 mg/L Zn(II) and 5.05 mg/L Cu(II)

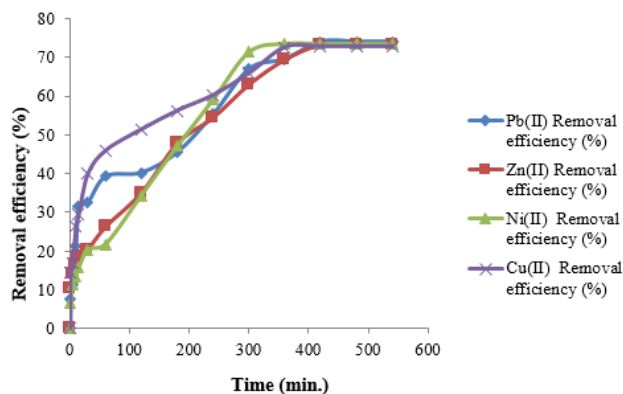


Fig. 11. Effect of time on removal efficiency (%) of Pb(II), Ni(II), Zn(II) and Cu(II) by glutaraldehyde-crosslinked chitosan from multi-metal solution with 90.72 mg/L Pb(II), 99.39 mg/L Ni(II), 92.32 mg/L Zn(II) and 108.8 mg/L Cu(II)

73.16 % for Zn(II), 73.45 % for Ni(II), and 72.77 % for Cu(II). These results lead to the conclusion that Chit-GLA beads have good sorption capacity and selectivity for Cu(II). The following selectivity series can be drawn: Cu(II) > Zn(II) > Ni(II) > Pb(II). The time to reach the equilibrium is 360-420 minutes. Consequently, Pb(II), Ni(II), Zn(II) and Cu(II) removal by Chit-GLA beads from multi-metal solutions can be considered as a fast process.

Effect of glutaraldehyde concentration on Pb(II), Ni(II), Zn(II) and Cu(II) removal process by Chit-GLA beads

In order to determine the effect of GLA concentration on sorption capacity, batch experiments were carried out using Chit-GLA beads obtained by the use of GLA solutions with different concentrations. Thus, Chit-GLA beads were obtained by the method described in our previous studies [14] using GLA 0.1%, GLA 0.5%, GLA 1%, and GLA 2%.

A volume of 50 mL multi-metal 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) was contacted with 0.05 g Chit-GLA 0.1% beads for 480 min at 150 rpm and room temperature. The same sorption process conditions was used in sorption experiments performed with Chit-GLA 0.5%, Chit-GLA 1% and Chit-GLA 2% beads. The results obtained are shown in figure 12.

From the figure 12, it is noticeable that GLA concentration has an important effect on sorption capacity of Chit-GLA copolymers. A higher concentration of GLA determines decreasing of Chit-GLA sorption capacity. This can be due to the fact that, Chit-GLA copolymers are obtained by a Schiff base reaction between $-NH_2$ groups of chitosan and $C=O$ groups of glutaraldehyde. By this reaction, the free $-NH_2$ will not be available for metal ions bonding, and thus the sorption capacity will decrease. This

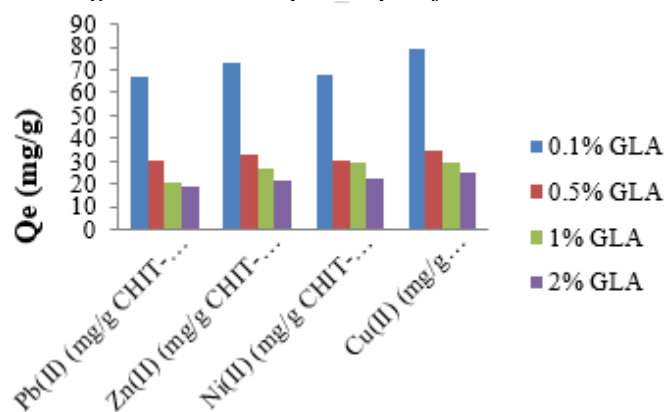


Fig. 12. The effect of GLA concentration on sorption capacity of Chit-GLA beads

conclusion is in agreement with other research studies [14, 16].

Adsorption isotherm

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 is described by adsorption isotherms [15]. The known Langmuir and Freundlich isotherms models were used to describe the equilibrium data of Pb(II), Zn(II), Ni(II) and Cu(II) sorption onto Chit-GLA beads.

Based the Langmuir model, the metal uptake process takes place on the surface of adsorbent in a homogeneous monolayer distribution without any type of interaction between adsorbed ions [15]. Mathematically, the Langmuir model is expressed by the following equation (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 [17].

The Freundlich isotherm assumes sorption on a heterogeneous surface. According to this model, the stronger binding sites are occupied first, and then the bonding strengths will decreased with increasing degree of site occupation [18]. Equation (4) represents the mathematically expression of the Freundlich model [18].

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

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 following:

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

The adsorption linearized isotherms for Pb(II), Ni(II), Zn(II) and Cu(II) sorption on chit-GLA are shown in figures 13 and 14. The Langmuir and Freundlich parameters were determined from these plots, and they are presented in table 1.

According to the values of correlation coefficient (R^2) presented in table 1 the Langmuir model adequately described the sorption process for Pb(II), Ni(II), Zn(II), and Cu(II) from multi-metal systems. Thus, it can be concluded that Langmuir isotherm could be considered as a better fitting model than Freundlich model for Pb(II), Ni(II), Zn(II), and Cu(II) sorption on Chit-GLA beads. This indicates that removal process takes place as sorption of Pb(II), Ni(II), Zn(II) and Cu(II) on the surface of Chit-GLA in a homogeneous monolayer distribution without any type of interaction between Pb(II), Ni(II), Zn(II) and Cu(II) adsorbed ions [15].

Adsorption kinetics

A kinetic study was carried out to quantify the adsorption rate controlling steps in Pb(II), Ni(II), Zn(II) and Cu(II) uptake from multi-metal systems on Chit-GLA beads. The pseudo-first-order, the pseudo-second-order and intraparticle diffusion kinetic models were applied for this kinetic study.

According to pseudo-first-order model introduced by Lagergren (eq.6) the rate of adsorption on sorbent is proportional to the number of active sites available onto adsorbent [19].

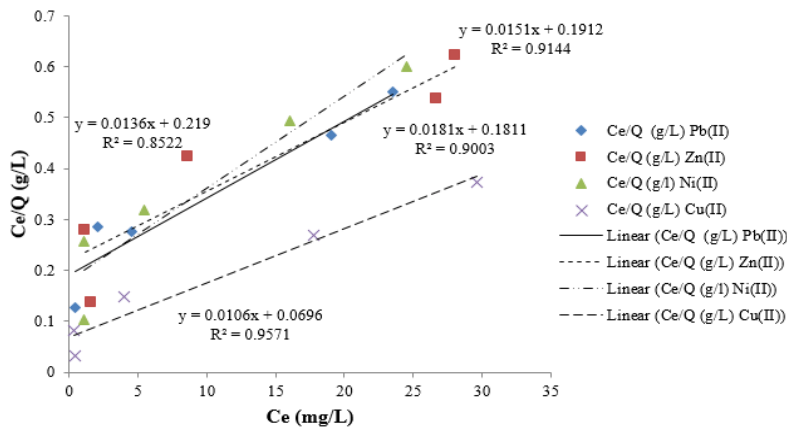


Fig 13. Langmuir linearised sorption isotherms of lead, nickel, zinc and copper from multi-metal systems

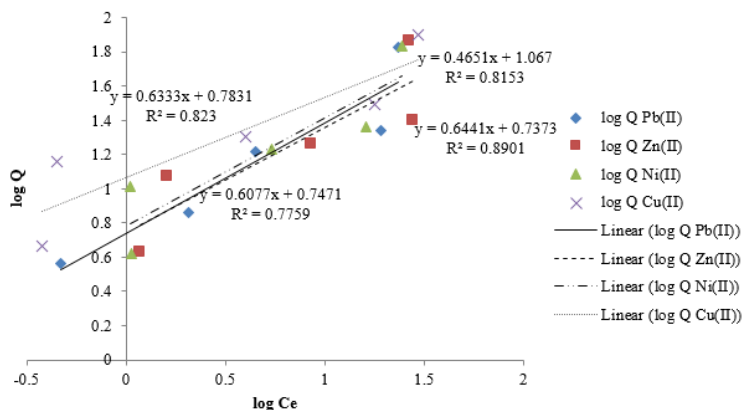


Fig 14. Freundlich linearised sorption isotherms of lead, nickel, zinc and copper from multi-metal systems

Table 1

LANGMUIR AND FEUNDLICH PARAMETERS FOR Pb(II), Ni(II), Zn(II) AND Cu(II) SORPTION BY CHIT-GLA FROM MULTI-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)	66.67	0.0785	0.914	11.669	2.1505	0.815
Ni(II)	55.56	0.0994	0.900	5.46	1.5528	0.890
Zn(II)	76.92	0.0594	0.852	5.59	1.6474	0.775
Cu(II)	100	0.1449	0.957	6.08	1.5798	0.823

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

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 linear form of the equation (6) is represented by equation (7) that 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 represent the amount of Pb(II), Ni(II), Zn(II) and Cu(II) adsorbed onto Chit-GLA (mg/g) at equilibrium and at time t , respectively and k_1 is the rate constant of first-order sorption (min^{-1}).

The slope and intercept of the liner plot of $\log(Q_e - Q_t)$ versus t (fig. 15) have been used to determine 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 onto Chit-GLA.

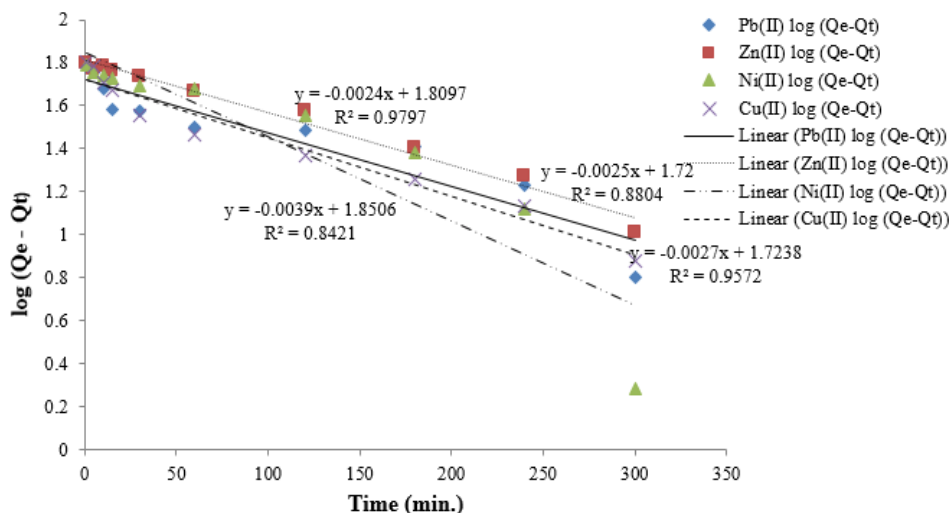


Fig. 15. Pseudo-first order sorption kinetics of Pb(II), Ni(II), Zn(II) and Cu(II) from multi-metal aqueous system onto Chit-GLA

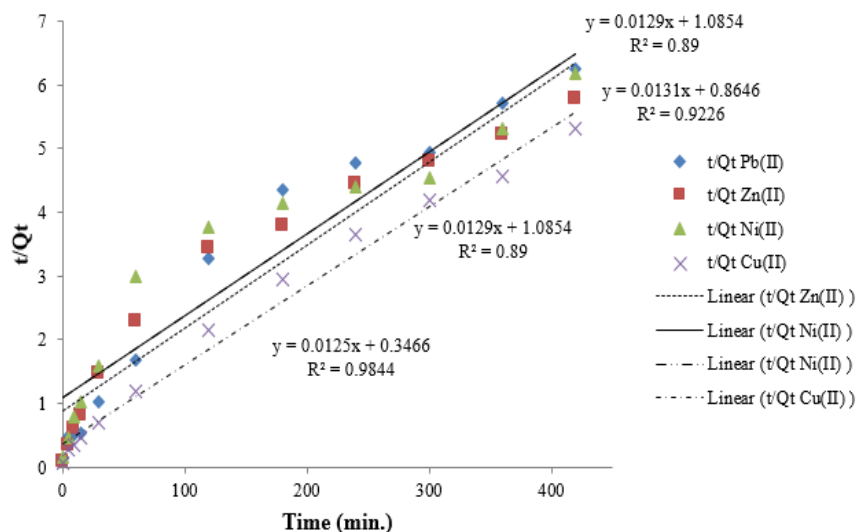


Fig. 16. Pseudo-second order sorption kinetics of Pb(II), Ni(II), Zn(II) and Cu(II) from multi-metal aqueous systems onto Chit-GLA

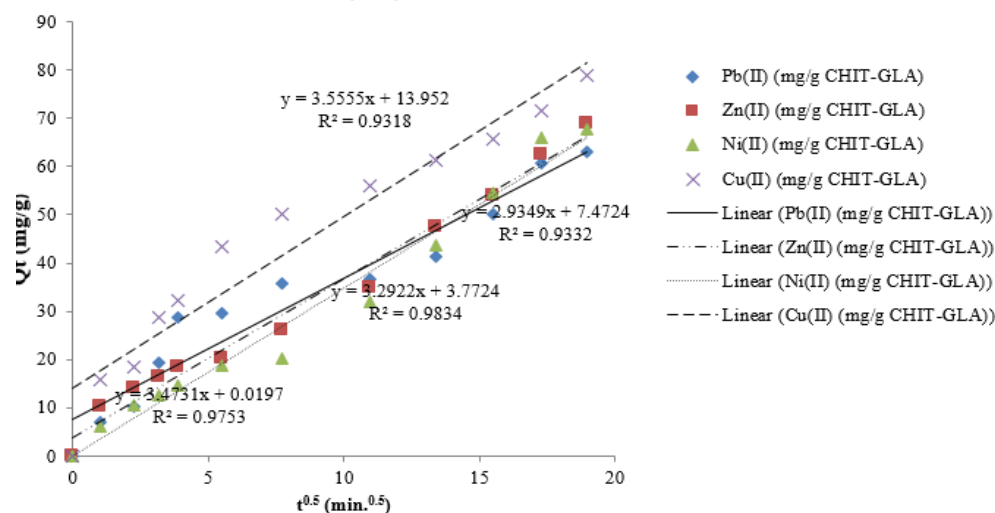


Fig. 17. Intraparticle diffusion sorption kinetics of Pb(II), Ni(II), Zn(II) and Cu(II) onto Chit-GLA

Table 3

THE RATE CONSTANT AND R² CORRELATION COEFFICIENT VALUES FOR Pb(II), Ni(II), Zn(II) AND Cu(II) SORPTION ONTO CHIT-GLA

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)	4.606·10 ⁻²	0.880	1.3272·10 ⁻⁴	0.89	2.934	0.933
Ni(II)	6.909·10 ⁻²	0.842	1.9562·10 ⁻⁴	0.922	3.473	0.975
Zn(II)	4.606·10 ⁻²	0.979	1.3272·10 ⁻⁴	0.89	3.292	0.983
Cu(II)	4.606·10 ⁻²	0.957	4.1622·10 ⁻⁴	0.984	3.555	0.931

The pseudo-second-order model [20] expressed by the equation (8) is based on 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: k₂ is the rate constant of second-order adsorption (g/mg·min). The values of k₂ and Q_e have been determined by the linear plot of t/Q_t versus t (fig. 16).

Intraparticle diffusion model (9) applied to explain the diffusion mechanism is expressed by the following equation [21]:

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

where k_i is intraparticle diffusion rate (mg/g·min). The slope of straight-line portions of the plot of Q_t against t^{0.5} (fig 17) has been used to determine the values of k_i.

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

By analysing the data presented in figures 15 - 17 and table 3, it can be concluded that intraparticle diffusion is in better agreement with experimental data regarding the

kinetics of Pb(II), Ni(II), and Zn(II) ions sorption on Chit-GLA compared to pseudo-first-order and pseudo-second-order kinetic models. In case of Cu(II) ions sorption onto Chit-GLA the rate determining step is chemical adsorption and not physical sorption and the mass transfer due to the fact that this sorption process can be described better by pseudo-second-order kinetic model.

Conclusions

The chemical modification of chitosan flakes was performed in order to obtain a sorbent with better sorption capacity and higher stability in solutions. This sorbent was tested for Pb(II), Ni(II), Zn(II) and Cu(II) ions from multi-metal aqueous solutions removal processes. Optimum removal for all metal ions was obtained at pH in the range 5.2-5.6 and a contact time of 360-420 min. The concentration of GLA used to obtain Chit-GLA copolymers has effect on Chit-GLA sorption capacity. The experimental results were analyzed using the Langmuir and Freundlich adsorption models. The Langmuir model gave the best fit to the experimental data for all four metals tested. The kinetic data followed the intraparticle diffusion for Pb(II), Ni(II) and Zn(II), and pseudo-second-order kinetic for Cu(II).

Thus Pb(II), Ni(II), and Zn(II) sorption onto Chit-GLA can be described as diffusion process and as chemisorptions for Cu(II). The results of this investigation showed that Chit-GLA can be used as an effective adsorbent of Pb(II), Ni(II), Zn(II) and Cu(II) removal from multi-metal aqueous solutions and wastewater. The following series of the selectivity of Chit-GLA sorbent can be proposed: Cu(II) > Zn(II) > Ni(II) > Pb(II).

Acknowledgments: The research was financed by the Ministry of National Education – Executive Unit for Financing Higher Education, Research and Development and Innovation (MEN – UEFISCDI) in the PARTNERSHIP in the priority areas PNII program through project PARTNERSHIP 92/01.07.2014.

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Manuscript received: 15.12.2015