The Kinetic and Modeling Study of Zinc Sorption onto Chitosan-glutaraldehyde Beads

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The aim of this research study was to investigate the effectiveness of chitosan beads chemically by crosslinking with glutaraldehyde in zinc removal from aqueous solutions. The effect of the followings parameters such as: glutaraldehyde concentration used in obtaining copolymers, zinc level in initial solution, time, and pH value was investigated. The equilibrium data were evaluated using Langmuir and Freundlich isotherm models. The kinetics was analyzed with the pseudo-first-order rate equation, the pseudo-second-order rate equation and intraparticle diffusion. The results of this research study can lead to the conclusion that chitosan-glutaraldehyde can be used as a cost-effective material for the removal of zinc from aqueous solutions and wastewater.

Keywords: zinc removal, zinc sorption, chitosan chemical modification

Zinc is considered an essential element for human body, but in high levels it has acute effects such as nausea, vomiting, diarrhea, loss of appetite, headaches, and also chronic effects including low copper status, reduced immune function, reduced levels of high-density lipoproteins, and altered iron function [1]. It can enters in environment with effluents from electroplating baths, acid mine drainage, municipal wastewater treatment plants, natural ores, rayon, yarn and fiber manufacture, steelworks, ground wood-pulp production, recirculation cooling water systems, and metal processing industry [2,3]. Like other metals, zinc is not biodegradable and travels through the food chain via bioaccumulation [3]. Consequently, there is a growing interest related to zinc removal from wastewaters. Numerous traditional methods such as chemical precipitation [4], ion exchange [5], reverse osmosis [6], sequestration [7], coagulation-flocculation [8], solvent extraction [9], electrocoagulation [10], filtration [11], adsorption [12] have been used for zinc removal. Each of these methods has advantages and disadvantages.

Biosorption is an unconventional method for heavy metal removal from wastewater that has been extended studied recently due to its numerous advantages such as low cost, high efficiency, minimization of heavy metals even at low concentration in wastewater, regeneration of biosorbent, and possibility of heavy metals recovery [13-15]. Many biosorbents such as seafood waste, egg shells, coconut husks, rice husks, palm fruits, nut shells, fruit bagasse, yeasts, fungal and bacterial biomass, algae have been tested in heavy metals removal from wastewaters [13-18]. Numerous research studies have been performed to obtain various suitable or new sorbents/adsorbents/biosorbents for heavy metal removal from aqueous solution [19].

Chitin and chitosan have been widely used in many fields such as biomedical, pharmaceutical, food preservatives, microbiological and environmental protection [20, 21]. Physical and chemical or hybrids chitosan modifications have been reported to increase its stability in acid media, to obtain good mechanical properties, to enhance the metal sorption properties, and to improve separation from real/synthetic effluents after treatment. For these purposes many crosslinking/grafting agents such as crown ether, cyclodextrins (CDs), EDTA/DTPA, sugars, magnetite, thiourea, thiocarbamoyl, L-lysine, glycineethylenediamine, glutaraldehyde, hexamethylene, diisocyanate and epichlorohydrin have been used [19].

Due to the fact that chitosan can be easily modified to obtain desirable sorbents with increased sorption capacity and selectivity for heavy metals, the present study was undertaken to evaluate the effectiveness of chitosan-glutaraldehyde sorbents in zinc removal from synthetic aqueous solutions. The chitosan-glutaraldehyde sorbents (Chit-GLA) were characterized in other previous study [22].

Experimental part

Materials and testing equipments

The chitosan-glutaraldehyde sorbents (Chit-GLA) beads with low solubility in acidic solutions, and sorption capacity were obtained according to a method first time reported by Ngah and Fatinathan [23]. Chit-GLA 0.5% represents Chit-GLA particles obtained by use 0.5% glutardialdehyde solution, Chit-GLA 1% are Chit-GLA particles obtained by use 1% glutardialdehyde solution, and Chit-GLA 2% represents Chit-GLA particles obtained by use 2% glutardialdehyde solution. 1000 mg/L stock zinc(II) solution was prepared by dissolving 4.5986 g of $ZnSO_4 \cdot 7H_2O$ (Merck) in 1L distilled water. The required concentration of Zn(II) solution was obtained by serial dilution of 1000 mg/L Zn(II) solution. 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. Zinc ions concentration in the initial solutions and in solutions after the sorption on Chit-GLA was determined by atomic absorption spectrometry by

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the use of an AAS 1N Carl Zeiss Jena Atomic Adsorption Spectrophotometer. The two phases (solid – Chit-GLA and liquid – zinc synthetic solutions) were put in contact by the use of a GFL Shaker 3015 at 150 rpm. The solution *p*H was determined with an Agilent 3200 laboratory pH-meter.

Sorption experiments

Sorption batch experiments were performed to test sorption capacity of chitosan-GLA particles in function of GLA concentration in the removal of Zn(II) from aqueous solutions. Experiments were performed by diluting the stock solutions of Zn(II) to desired concentrations (6.22 mg/L, 15.39 mg/L, 39.5 mg/L, 85.05 mg/L, and 167.8 mg/L).

The effect of the contact time on the sorption of Cu(II) ions was conducted by contacting 0.025 g of Chit-GLA with 25 mL of zinc ions solution at room temperature (21 ± 2°C). The contact time varied between 5 and 480 minutes. The initial *p*H was other parameter that was investigated. The *p*H range studied was 2-6. The sorbent was stirred with the Zn(II) ions solution at 150 rpm for 480 min.

The amount of zinc ions adsorbed by Chit-GLA particles (mg/g) was calculated using eqs. (1):

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

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

Results and discussions

Effect of pH on zinc removal process by Chit-GLA copolymers

*p*H represents one of the parameters with important influence on the metal ions adsorption process. It controls the nature of ionic species presented in the solution. For this reason, the role of the hydrogen ion concentration was investigated in the current work by the use zinc solutions with *p*H values ranging from 2 to 6. Higher values of *p*H have not been chosen for experiments because the zinc hydroxyl components are the dominant species in the range of 7-12. Thus, these species can hinder the direct interaction between zinc ions and the active sites of Chit-GLA 0.5%. Chit-GLA 0.5% was chosen to establish the influence of *p*H on zinc removal by chitosan-glutaraldehyde copolymers due to the fact that in our previous experiments it was concluded that increased glutaraldehyde concentrations determine decreasing the sorption capacity of Chit-GLA copolymers.

The relation between the initial *p*H of the solution and the amount of Zn(II) retained by the micro and Chit-GLA 0.5% particles is shown in the figure 1 for different zinc concentrations.

From this figure it can be observed that in the lower initial *p*H range the amount of zinc adsorbed by Chit-GLA 0.5% particles increases with the increasing of *p*H value till it reaches a maximum value. The low values of adsorption at very low *p*H values could be the result of the competition between protons and zinc ions at the sorption sites, with a preponderance of protons which hinder the approach of zinc ions as a result of repulsive forces. The maximum sorption capacity was reached at *p*H 5.62 - 5.8. This finding is consistent with literature data [24]. At *p*H higher than 6 some other phenomena such as precipitation of $Zn(OH)_2$ can occur, and thus further investigation of Zn adsorption for *p*H values higher of 6 is not recommended [24].

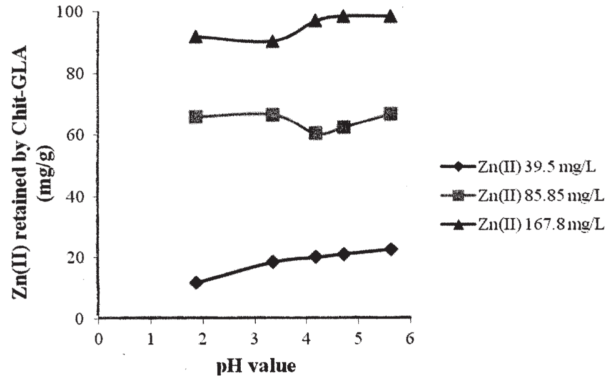

Fig. 1. Influence of *p*H on the Zn(II) amount retained by Chit-GLA 0.5% at different concentrations of the initial solution.

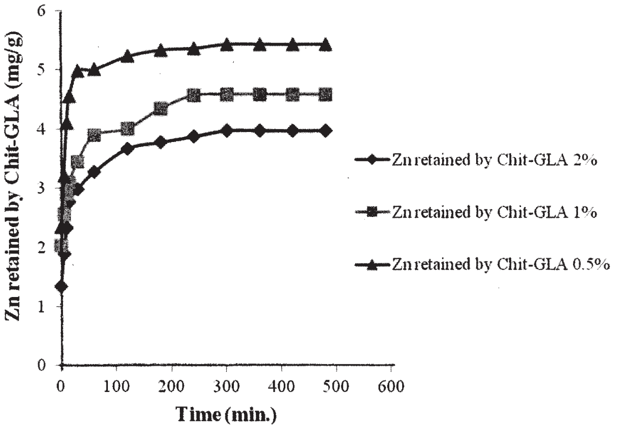

Fig. 2. Time effect on Zn(II) sorption on Chit-GLA from 6.22 mg/L Zn(II) solution

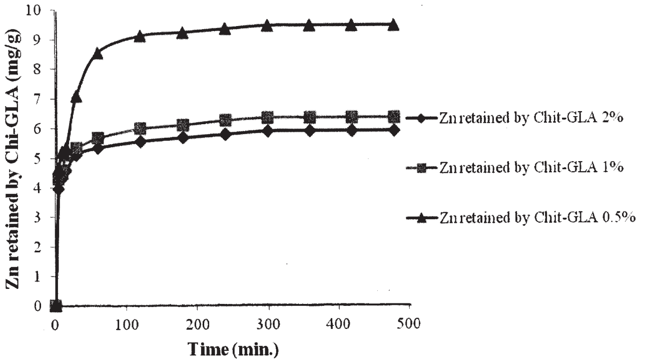

Fig. 3. Time effect on Zn(II) sorption on Chit-GLA from 15.39 mg/L Zn(II) solution

The results of these experiments will be used in the further kinetic and modeling experiments. Thus, the next studies have been performed without adjusting the initial solution *p*H value due to the fact that it is in the range 5.62-5.8.

Effect of time and GLA concentration on zinc removal process by Chit-GLA copolymers

Batch experiments have been performed in order to determine the equilibrium time, and sorption capacity of Chit-GLA copolymers. The results obtained regarding the effect of the contact time on zinc sorption process are presented in the following figures for all zinc concentration chosen.

The figures 2-6 revealed that increasing of the contact time determines the increasing of the Zn(II) quantity removed by Chit-GLA. In our experiments, the time to reach the equilibrium is about 5 h. The time to reach the

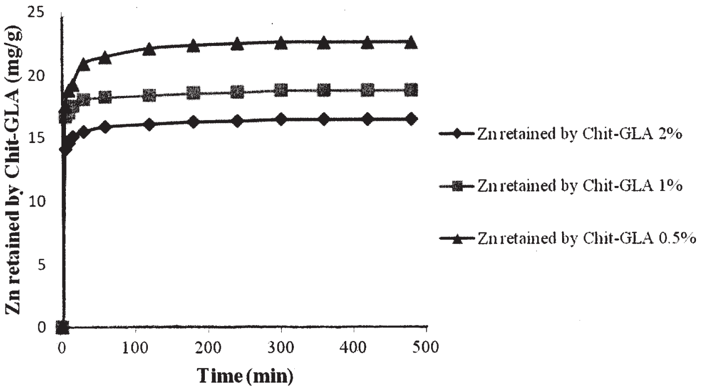

Fig. 4. Time effect on Zn(II) sorption on Chit-GLA from 39.5 mg/L Zn(II) solution

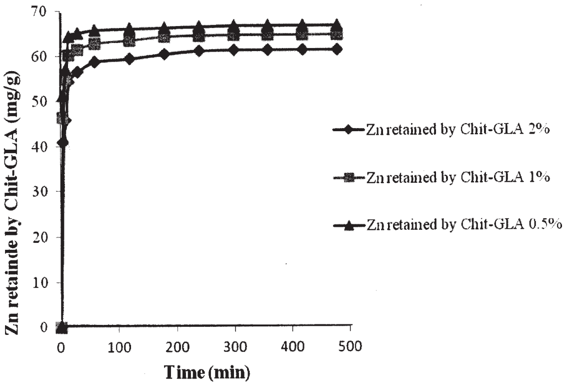

Fig. 5. Time effect on Zn(II) sorption on Chit-GLA from 85.05 mg/L Zn(II) solution

equilibrium is an important factor that will be taken in consideration when the laboratory experiments will be used to design a pilot wastewater treatment system and/ or an industrial wastewater treatment system.

Another conclusion that can be drawn from the figures 2-6 is that the increasing of GLA concentration has as effect the decreasing of the Zn(II) quantity removed by Chit-GLA. The sorption capacity of Chit-GLA determined by these experiments has a value of 98.4 mg/g. This value is consistent with the literature data presented in the table 1.

Adsorption isotherm models

The Langmuir and Freundlich adsorption isotherm models were used to fit the experimental results and calculate the maximum theoretical adsorption capacities. At first, the equilibrium results were fitted to Langmuir equation presented in the equation (2);

$$\frac{C_e}{Q} = \frac{1}{K_L} + \left(\frac{a}{K_L}\right) \cdot C_e \qquad (2)$$

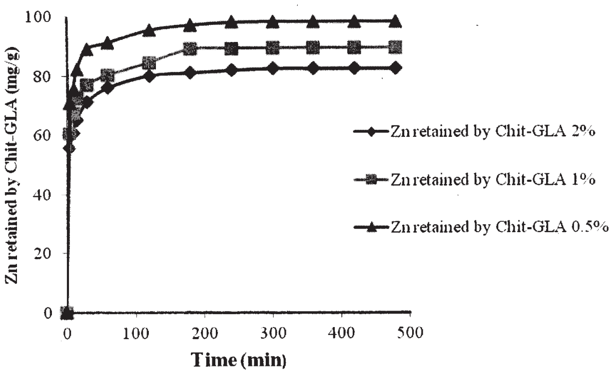

Fig. 6. Time effect on Zn(II) sorption on Chit-GLA from 167.8 mg/L Zn(II) solution

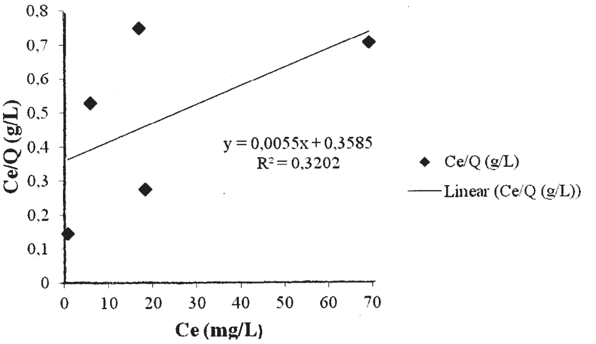

Fig. 7. Langmuir linearized isotherm for zinc sorption on Chit-GLA

where

Q - the maximum adsorption at monolayer (mg/g); C_e - the equilibrium concentration of Zn(II) (mg/L); K_L and *a* are the Langmuir model parameters [34]. Figure 7 has been used to determine values of Langmuir parameters (K_L and a) for zinc sorption on Chit-GLA.

Freundlich isotherm equation (3) was used to fit the experimental results [35]:

$$Q = K_F \cdot C_e^{1/n} \qquad (3)$$

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

By logarithmation, the equation (3) will be:

$$\log Q = \log K_F + \tfrac{1}{n}\log C_e \qquad (4)$$

The Freundlich linearized isotherm for zinc sorption on Chit-GLA is presented in figure 8. This has been used to determine the Feundlich parameters.

Table 1
COMPARISON OF ADSORPTION CAPACITIES FOR THE REMOVAL OF ZINC FROM AQUEOUS SOLUTIONS USING CHITOSAN-BASED ADSORBENTS

Adsorbent	Q (mg/g)	References
Chitosan flakes	117.7	[25]
Hydroxyapatite/chitosan composite	110	[26]
Chitosan cross-linked with epichlorohydrin	10	[27]
Chitosan grafted with a-ketoglutaric acid	20	[28]
Magnetic chitosan cross-linked with glutaraldehyde	32	[29]
Magnetic chitosan modified with diethylenetriamine	180	[30]
Cross-linked modified chitosan-thioglyceraldehyde	52	[31]
Cross-linked magnetic chitosan-phenylthiourea	52	[32]
Xanthate-modified magnetic chitosan	21	[33]
Succinyl-grafted chitosan	178	[24]

Table 2
LANGMUIR AND FREUNDLICH SORPTION PARAMETERS FOR ZINC SORPTION ON CHIT-GLA COPOLYMER

Sorbent	Langmuir parameters			Freundlich parameters		
	K_L (L/mg)	a (mL/mg)	R^2	K_F (mg/g)	n	R^2
Chit-GLA	2.7933	$1.4\cdot10^{-2}$	0.320	4.396	1.6807	0.838

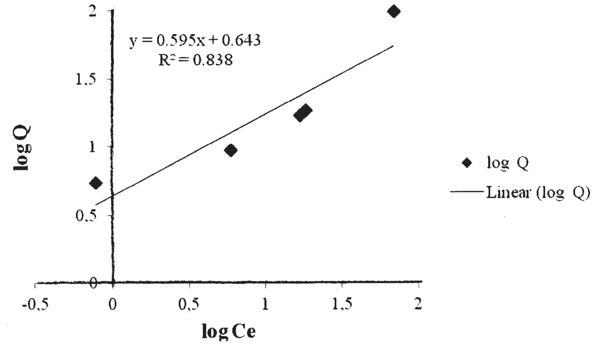

Fig. 8. Freundlich linearized isotherm for zinc sorption on Chit-GLA

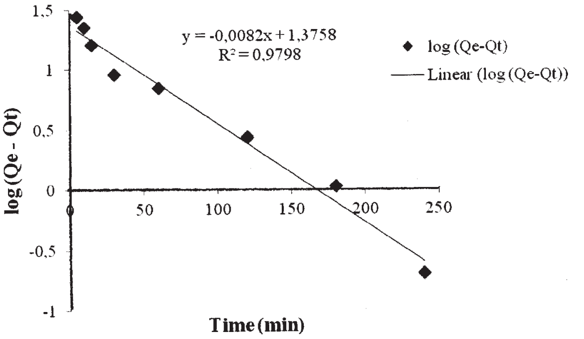

Fig. 9. Pseudo-first order sorption kinetics Zn(II) onto Chit-GLA 0.5%

All isothermal parameters resulted from the Langmuir and Freudlich fitting are reported in table 2. From the analysis of values presented in table 2 and figure 7 - 8 it can be concluded that the experimental data were better fitted to Freudlich equation ($R^2 = 0.838$) than to Langmuir equation ($R^2 = 0.320$). Thus, the adsorption behavior follows the Freudlich adsorption isotherm with maximum adsorption capacity of 4.396 mg/g and a Freudlich adsorption equilibrium constant of 1.6807 at room temperature. Thus, it can be concluded that zinc sorption onto Chit-GLA can be described by Freundlich isotherm that indicates that adsorption goes off as a multi-site adsorption.

Adsorption kinetic

The kinetic studies were performed by contacting samples containing Chit-GLA 0.5% and Zn(II) solutions at time from 5 min to 480 min. These experiments were performed in order to verify sorption kinetic models.

The evaluation of adsorption kinetics was based on fitting to pseudo-first order equation, pseudo-second order equation, and intraparticle equation which are characterized as the most successful kinetic models. These were used also to establish the mechanism of sorption and potential rate controlling steps. These parameters are useful tools for selecting optimum operating conditions for the full-scale batch process.

According to pseudo-first-order model presented by Lagergren equation (5), the rate of adsorption on sorbent is proportional to the number of active sites available onto adsorbent media [35].

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \qquad (5)$$

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 analysis of the kinetic data was done according to the linear form of the Lagergren model as follows:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}\cdot t \qquad (6)$$

where Q_e and Q_t represent the amount of Zn(II) sorbed on Chit-GLA 0.5% (mg/g) at equilibrium and at time t, respectively and k_1 is the rate constant of first-order sorption (min^{-1}). Rate constant, k_1 and correlation coefficient, R, values for Zn(II) sorption were determined from the graphic $\log(Q_e\text{-}Q_t) = f(t)$ (fig. 9).

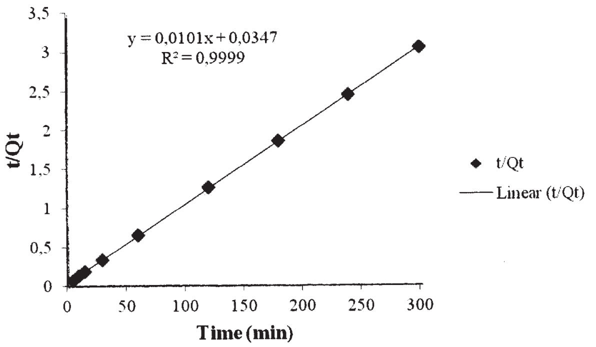

Fig. 10. Pseudo-second order sorption kinetics Zn(II) onto Chit-GLA 0.5%

The second-order model [35] is represented by the equation:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \qquad (7)$$

where: k_2 is the rate constant of second-order adsorption (g/mg·min). Straight-line plots t/Q_t against t (fig. 10) was used to express the kinetic parameters. The results have been used to determine the applicability of the second-order kinetic model to the experimental data.

The following equation is used to determine the intraparticle diffusion rate [36] :

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

where k_i is intraparticle 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 ZnII) sorption on Chit-GLA 0.5% is presented in figure 11.

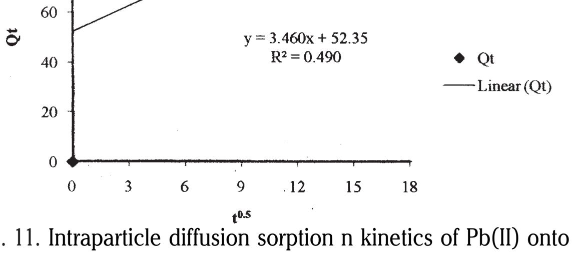

Fig. 11. Intraparticle diffusion sorption n kinetics of Pb(II) onto Chit-GLA 0.5%

Table 3
THE RATE CONSTANT AND R^2 CORRELATION COEFFICIENT VALUES FOR ZN(II) SORPTION ONTO CHIT-GLA 0.5%

Sorbent	**Pseudo-first order sorption**		**Pseudo-second order sorption**		**Intraparticle difussion**	
	k_1 (min^{-1})	R^2	k_2 (g/mg·min)	R^2	k_i (mg/mg·$min^{0.5}$)	R^2
Chit-GLA 0.5%	$1.8424 \cdot 10^{-2}$	0.979	$2.9412 \cdot 10^{-3}$	0.999	3.46	0.490

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

Table 3 shows that pseudo-second-order model is in better agreement with experimental data regarding the kinetics of Zn(II) ions sorption on Chit-GLA 0.5% 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 because the correlation coefficient (R^2 is equal with 0.999).

Conclusions

The present research study investigates the use of chitosan-glutaraldehyde copolymer (Chit-GLA) as adsorbent for removal of Zn(II) from aqueous solutions. Batch experiments were performed in order to establish the factors that influence the sorption process. The optimum *p*H value found after ph-effect experiments was 5.62-5.8. The maximum sorption capacity determined experimentally was 98.4 mg/g. The comparative study regarding the establish the effect of the GLA concentration to the sorption capacity showed that increasing the GLA concentration determines the decreasing of sorption capacity. Equilibrium data were fitted to Langmuir and Freundlich isotherm. The experimental data showed that the zinc sorption onto Chit-GLA can be described by Freundlich isotherm that indicates that adsorption goes off as a multi-site adsorption. The pseudo-second order best describes the Zn(II) adsorption process, which assumes that chemisorption is the rate controlling mechanism. The value of sorption capacity recommends Chit-GLA copolymer as an effective adsorbent in Zn(II) removal from aqueous solutions and wastewater.

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: 10.08.2015