

Efficiency of Chitosan for the Removal of Pb (II), Fe (II) and Cu (II) Ions from Aqueous Solutions

Soheil Sobhanardakani*¹, Raziye Zandipak², Hassan Parvizimosaed², Arash Javanshir Khoei³, Mehran Moslemi⁴, Mahsa Tahergorabi⁵, Seyed Mehdi Hosseini⁶, Parisa Delfieh⁷

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ABSTRACT

Background: Heavy metals have been recognized as harmful environmental pollutant known to produce highly toxic effects on different organs and systems of both humans and animals. The aim of this paper is to evaluate the adsorption potential of chitosan for the removal of Pb(II), Fe(II) and Cu(II) ions from aqueous solutions.

Methods: This study was conducted in laboratory scale. In this paper chitosan has been used as an adsorbent for the removal of Pb(II), Fe(II) and Cu(II) from aqueous solution. In batch tests, the effects of parameters like pH solution (1.0-8.0), initial metal concentrations (100-1000 mgL⁻¹), contact time (5.0-150 min) and adsorbent dose (1.0-7.0 g) on the adsorption process were studied.

Results: The results showed that the adsorption of Pb(II), Fe(II) and Cu(II) ions on chitosan strongly depends on pH. The experimental isothermal data were analyzed using the Langmuir and Freundlich equations and it was found that the removal process followed the Langmuir isotherm and maximum adsorption capacity for the adsorption of Pb(II), Fe(II) and Cu(II) ions by the chitosan were 55.5mg g⁻¹, 71.4 mg g⁻¹ and 59 mg g⁻¹, respectively, under equilibrium conditions at 25±1 °C. The adsorption process was found to be well described by the pseudo-second-order rate model.

Conclusion: The obtained results showed that chitosan is a readily, available, economic adsorbent and was found suitable for removing Pb(II), Fe(II) and Cu(II) ions from aqueous solution.

Keywords: Adsorption, Chemical Water Pollution, Chitosan, Heavy Metals, Removal Efficiency.

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INTRODUCTION

Heavy metals pollution is one of the most significant environment problems, since they are non-degradable and can accumulate in the food chain and hence in the human body [1]. Industrial and mining wastewaters are important sources of heavy metals pollution [2, 3]. Heavy metals including copper and lead are also toxic for plants and can affect the root growth [4]. Industrial processes such as mining, electroplating, dyeing, paper and petroleum produce wastewaters containing heavy metals that are toxic to living organisms [5]. Copper can cause

hemolysis, liver and kidney damage, irritation of upper respiratory tract, gastrointestinal disturbance and diarrhea. Lead can cause anaemia, kidney disease and mental retardation [6, 7].

Many treatment processes, such as oxidation, reduction, precipitation, membrane filtration, ion exchange and adsorption have been used to remove metal ions from aqueous solutions [8]. Among the above methods, adsorption is simple and cost-effective, thus has been widely used [9]. One of the low-cost adsorbents is chitosan (CS). It is a type of natural polyaminosaccharide, synthesized from

1. Department of the Environment, College of Basic Sciences, Hamedan Branch, Islamic Azad University, Hamedan, Iran.

2. MSc Environment, Young Researchers & Elite Club, Hamedan Branch, Islamic Azad University, Hamedan, Iran.

3. Department of Fisheries, University of Tehran, Karaj, Iran.

4. Department of Fisheries, Islamic Azad University, Jouybar Branch, Jouybar, Iran.

5. Department of Public Health, Kerman University of Medical Sciences, Kerman, Iran.

6. Department of Natural Resources, Isfahan University of Technology, Isfahan, Iran.

7. Department of Fisheries, Khoramshar University of Marine Science and Technology, Khoramshar, Iran.

* Corresponding Author: E-mail: soheil_sobhan@yahoo.com

the deacetylation of chitin [10]. CS [poly- β (1,4)-2-amino-2-deoxy-D-glucose] is known as an ideal natural support for enzyme immobilization because of its special characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity, adsorptive properties, etc. Due to the presence of amino and hydroxyl groups, which can serve as the active sites, CS can be used as an adsorbent for heavy metals and dyes [11]. From the literature it is clear that CS can be used to remove numerous trace metals (Cu(II), Pb(II), U(VI), Cr(III), Cr(VI), Ni(II), Cd(II), Zn(II), Co(II), Fe(II), Mn(II), Pt(IV), Ir(III), Pd(II), V(V) and V(IV)) from wastewater. In previous studies, CS has been used in a variety of forms, which include CS beads, flakes and membranes [12-16].

In the present study, CS was used for the removal of Pb(II), Fe(II) and Cu(II) from aqueous solutions. The effect of pH, initial concentration, contact time and CS dose were investigated. Isotherm and kinetics of adsorption were evaluated.

MATERIALS AND METHODS

Reagents and Materials

CS (ash: 0.55%, moisture: 5.4%, deacetylation: 88%) was purchased from Sigma-Aldrich (South, Africa). Figure 1 show the structure of CS. Other substances including; $\text{Pb}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, hydrochloric acid (HCl) and sodium hydroxide (NaOH) with the highest purity available were purchased from Merck (Darmstadt, Germany). Double-distilled water was used in all experiments. This study was conducted in laboratory scale. Stock solution (1000 mg L^{-1}) of Pb(II), Fe(II) and Cu(II) were prepared by dissolving $\text{Pb}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in double-distilled water. The solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions.

Batch Adsorption Experiments

Six g of CS was added to 100 mL of 100 mg L^{-1} of Pb(II), Fe(II) and Cu(II) solutions, and the pH of the solution was adjusted at 6.0 with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH solutions and then the mixtures were agitated using a magnetic stirrer with a stirring speed of 160

r. min^{-1} for 60 min. Subsequently, the CS with adsorbed Pb(II), Fe(II) and Cu(II) were separated from the mixture using Whatman filter paper with a pore diameter of $42 \mu\text{m}$. The concentration of the Pb(II), Fe(II) and Cu(II) ions which remained in the solution were determined by inductively coupled plasma spectrometry (Verian710-Es Australia) and the concentration of the Pb(II), Fe(II) and Cu(II) ions remained in the adsorbent phase (q_e , mg g^{-1}) were calculated using the Eq. (1);

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (1)$$

Where C_0 and C_e are the initial and equilibrium Pb(II), Fe(II) and Cu(II) concentrations in solution, respectively (mg L^{-1}), V (L) is the volume of solution and W (g) is the weight of adsorbent [17].

For studying the effect of solution pH on Pb(II), Fe(II) and Cu(II) ions adsorption, experiments with different pHs (varying from 1.0 to 8.0) were conducted. To observe the effect of adsorbent dose on Pb(II), Fe(II) and Cu(II) ions adsorption, different amounts of adsorbent (varying from 1.0 to 7.0 g) were used. In order to investigate the effect of contact time on adsorption contact times of 5, 10, 20, 30, 40, 60, 90, 120 and 150 min were used.

Finally, the Pb(II), Fe(II) and Cu(II) removal ratio (R%) was calculated by the Eq. (2);

$$R (\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where C_0 and C_e (mg L^{-1}) were the initial and final Pb(II), Fe(II) and Cu(II) concentrations [18].

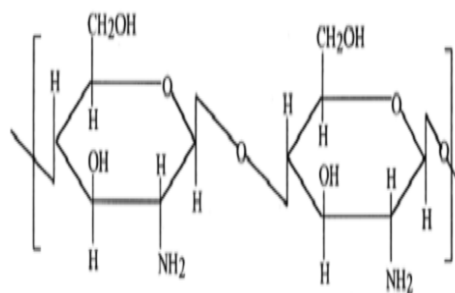


Figure 1. CS structure.

RESULTS

The primary study showed that the adsorption efficiency depends strongly on the solution pH, CS dose, contact time and temperature. To determine the optimum pH range for the removal of Pb(II), Fe(II) and Cu(II), the adsorption studies were carried out at different values, ranging from 1.0 to 8.0, with a stirring time of 60 min. As is seen in Figure 2, the removal efficiency increases and reaches maximum at 5.0 and 6.0 for Fe(II) and Cu(II), respectively and then remained nearly constant at higher pHs. Also the removal of Pb(II) increased from 12% to 86% when the pH increased from 1.0 to 6.0 and then decreases at pH 6.0–8.0.

The removal of Pb(II), Fe(II) and Cu(II) ions onto CS as a function of their concentrations was studied at constant temperature ($25 \pm 0.1^\circ\text{C}$) by varying the metals concentration from 100 to 1000 mgL^{-1} , while keeping all other parameters constant. The adsorption results of Pb(II), Fe(II) and Cu(II) by the CS are shown in Figure 3. It was found that by increasing the initial metal concentration, the amount of metal removal decreased.

Figure 4, shows the removal ratio of Pb(II), Fe(II) and Cu(II) ions at various time intervals onto CS from the aqueous solution. The uptake of metals by CS increased with increasing contact time and then became constant.

The dependence of the adsorption of Pb(II), Fe(II) and Cu(II) ions to the amount of CS was studied at constant temperature ($25 \pm 1^\circ\text{C}$) by varying the adsorbent amount from 1.0 to 7.0 g in contact with 100 mg L^{-1} of Pb(II), Fe(II) and Cu(II). The effect of adsorbent dose on Pb(II), Fe(II) and Cu(II) removal percentage is shown in Figure 5.

Two different isotherms, Langmuir and Freundlich models, were applied in this study for analyzing experimental sorption equilibrium parameters to obtain some important information on the surface properties of the adsorbent and its affinity for the metals molecules. Figure 6 and Table 1 show the results of linear fitting in Langmuir and Freundlich isotherms for CS.

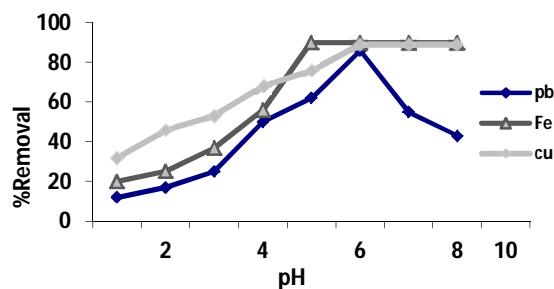


Figure 2. The effect of solution pH on the adsorption of Pb(II), Fe(II) and Cu(II) onto CS. (Initial metal concentration 100 mg L^{-1} , contact time 60 min, adsorbent dose 6.0 g, and temperature $25 \pm 1^\circ\text{C}$).

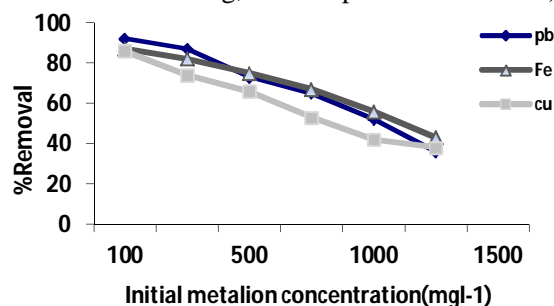


Figure 3. The effect of initial metal concentration on adsorption of Pb(II), Fe(II) and Cu(II) onto CS. (pH=6.0, 5.0 and 6.0 for Pb(II), Fe(II) and Cu(II) ions, respectively, contact time 60 min, adsorbent dose 6.0 g, and temperature $25 \pm 1^\circ\text{C}$).

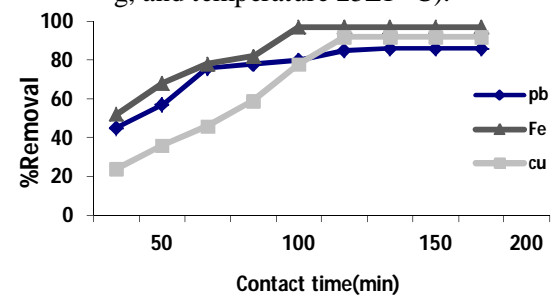


Figure 4. The effect of contact time on adsorption of Pb(II), Fe(II) and Cu(II) onto CS. (pH=6.0, 5.0 and 6.0 for Pb(II), Fe(II) and Cu(II) ions, respectively, initial metal concentration 100 mg L^{-1} , adsorbent dose 6.0 g, and temperature $25 \pm 1^\circ\text{C}$).

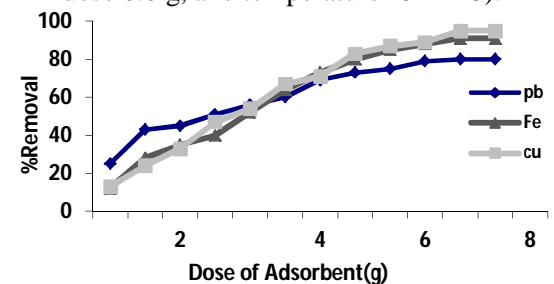
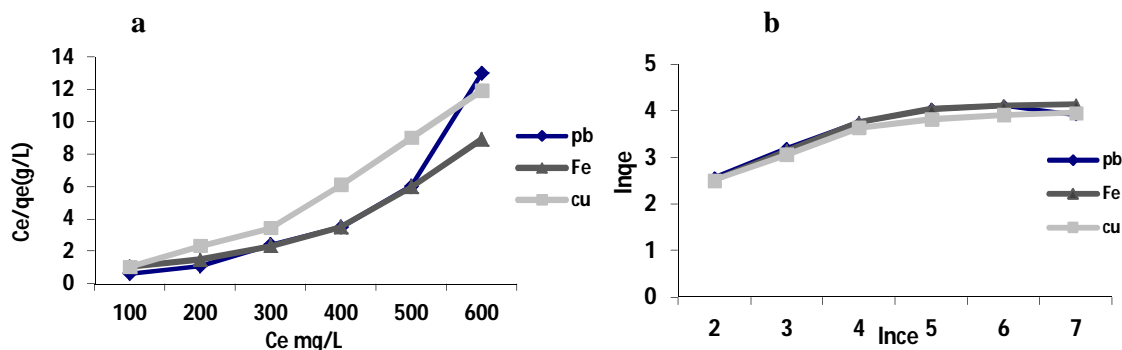


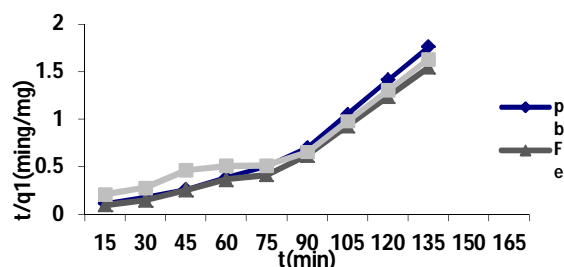
Figure 5. The effect of adsorbent dose on the adsorption of Pb(II), Fe(II) and Cu(II) onto CS. (pH=6.0, 5.0 and 6.0 for Pb(II), Fe(II) and Cu(II) ions, respectively, Initial metal concentration 100 mg L^{-1} , contact time 60 min, and temperature $25 \pm 1^\circ\text{C}$).

Table 1. Isotherm parameters of adsorption of Pb(II), Fe(II) and Cu(II) ions onto CS.

	Langmuir			Freundlich		
	b (L mg ⁻¹)	q _m (mg g ⁻¹)	R ²	K _f (mg ^{1-(1/n)} L ^{1/n} g ⁻¹)	n	R ²
Pb(II)	0.076	55.5	0.980	107.6	2.9	0.886
Fe(II)	0.016	55 71.4	0.998	33.5	2.2	0.942
Cu(II)	0.01	59	0.997	37.8	2.5	0.969

**Figure 6.** (a) Langmuir and (b) Freundlich isotherms for Pb(II), Fe(II) and Cu(II) ions adsorption onto CS.**Table 2.** Pseudo-first order and pseudo-second order kinetic model parameters for the adsorption of Pb(II), Fe(II) and Cu(II) ions onto CS.

	Pseudo-first-order kinetic model				Pseudo-second-order kinetic			
	C ₀ (mg L ⁻¹)	q _e exp (mg g ⁻¹)	q _{e1} (mg g ⁻¹)	k ₁ (min ⁻¹)	R ²	q _{e2} (mg g ⁻¹)	k ₂ (g mg ⁻¹ min ⁻¹)	R ²
Pb(II)	100	86	1.07	-0.025	0.754	90.9	0.002	0.999
Fe(II)	100	97	1.07	-0.026	0.623	111.1	0.001	0.998
Cu(II)	100	92	1.38	-0.033	0.782	109.3	0.004	0.985

**Figure 7.** Pseudo-second-order kinetics plot of Pb(II), Fe(II) and Cu(II) ions adsorption onto the CS.

DISCUSSION

The initial pH of solution plays an important role in the adsorption process and particularly on the adsorption capacity by controlling the surface charge of the adsorbent and the degree of ionization of the materials in the solution. The increase in the adsorption of Pb(II), Fe(II) and Cu(II) on CS with increase in the solution pH can be explained based on the surface charge of CS and the metal molecules. The results showed that the Pb(II), Fe(II) and Cu(II) removal was much higher in neutral pH. At lower pH, the CS surface will be positively charged, creating electrostatic repulsion between

the positively charged surface of the CS and the metals ions. At higher pH the number of positively charged sites is reduced and raised the number of negatively charged sites, which increases the electrostatic attractions between metals ions and CS surface. The effect of solution pH on the adsorption of metals could be explained by considering competition between H⁺ ions and Metal(II) ions for the active surface sites in acidic solutions. Similar phenomenon has also been shown in the adsorption of Pb(II) ion from water with kaolinite [19-21].

As in Figure 3 by increasing the initial concentration of Pb(II), Fe(II) and Cu(II) ions in

aqueous solution, the removal ratio of Pb(II), Fe(II) and Cu(II) ions were decreased, so that with a concentration of 100 mg L⁻¹ and constant contact time, the observed highest adsorption ratio and with an increase in the concentration from 100 to 1000 mg L⁻¹, the adsorption percentage decreased from 92% to 36% for Pb(II), 87% to 43% for Fe(II) and 86% to 38% for Cu(II). At a constant CS concentration, the decrease in the adsorption ratio is probably due to the saturation of the active sites on the CS surface at metal concentrations. On the other hand, by increasing the initial Pb(II), Fe(II) and Cu(II) concentrations the actual amount of metals adsorbed per unit mass of the CS increased. The higher initial concentrations of Pb(II), Fe(II) and Cu(II) provides an important driving force to overcome the mass transfer resistance for Pb(II), Fe(II) and Cu(II) transfer between the solutions and the surface of the CS. Similar results were observed by Ruis (2005) who investigated the effect of initial concentration of metals ions on the removal of Pb(II), Fe(II) and Cu(II) from aqueous solution by clay mineral montmorillonite and indicated that adsorption decreases with increasing initial concentrations of metals [22].

Equilibrium time is one of the most important parameters in the design of economical wastewater treatment systems. As can be seen, Pb(II) removal efficiency increased from 45% to 86% when contact time was increased from 5 to 60 min, Fe(II) removal efficiency increased from 52% to 97% when contact time was increased from 5 to 40 min and Cu(II) removal efficiency increased from 24% to 92% when contact time was increased from 5 to 60 min (Figure 4). The rapid adsorption at the initial contact time was due to the availability of more active surface of the adsorbents, which leads to fast adsorption of the Pb(II), Fe(II) and Cu(II) ions from the solution. The later slow rate of Pb(II), Fe(II) and Cu(II) ions adsorption probably occurred due to the lesser availability of active site on the surface of adsorbent as well as the slow pore diffusion of the solute into the adsorbent. Optimum contact time for CS adsorbent was found to be 60, 40, 60 min, respectively for Pb(II), Fe(II) and Cu(II) in the 100 mg L⁻¹ concentration. Similar results have been reported by Chen et al [23].

One of the parameters that strongly affect the adsorption capacity is the adsorbent dose. As it is clear from Figure 5, the removal ratio increased rapidly with an increase in the adsorbent dose up to 6.0 g, and afterwards 6.0 g, the removal ratio reached almost a constant value. This can be attributed to the increase in the adsorbent surface area and availability of more active adsorption sites on the CS surface with the increase in the amount of the adsorbent. Therefore, 6.0 g adsorbent was selected for subsequent work. This phenomenon was also observed by Madrakian et al. (2012), who studied the adsorption efficiency of uranium (VI) on modified maghemite nanoparticles and indicated that adsorption percentage increases with increasing adsorbent dose [24].

The equilibrium adsorption data of Pb(II), Fe(II) and Cu(II) ions onto CS adsorbent were analyzed using Langmuir and Freundlich models. The Langmuir isotherm Eq. (3) and Freundlich isotherm Eq. (4) can be expressed as follows [25].

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_1} \quad (3)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln k_f \quad (4)$$

where C_e (mg L⁻¹) is the equilibrium concentration of Pb(II), Fe(II) and Cu(II) ions in solution, q_e (mg g⁻¹) is the equilibrium adsorption capacity of CS, q_m (mg g⁻¹) is the maximum adsorption capacity of CS for monolayer coverage, b (L mg⁻¹) is a constant related to the adsorption free energy, K_f (mg^{1-(1/n)} L^{1/n} g⁻¹) is a constant related to adsorption capacity, and n is an empirical parameter related to adsorption. Figure 6a, b shows the equilibrium isotherms for the adsorption of Pb(II), Fe(II) and Cu(II) onto CS, and the parameters of adsorption isotherms are summarized in Table 1.

The higher correlation coefficient for Langmuir model indicated that the Langmuir model fitted the adsorption data better than the Freundlich model, which indicated the homogeneous distribution of active sites on the surface of CS. The results showed that the maximum adsorption capacity values for the adsorption of Pb(II), Fe(II) and Cu(II) ions by the CS were 55.5 mg g⁻¹, 71.4 mg g⁻¹ and 59 mg g⁻¹, respectively.

In order to analysis the adsorption mechanism of Pb(II), Fe(II) and Cu(II) ions onto CS, two kinetic models including the pseudo-first-order and the pseudo-second-order models were used. The linear form of pseudo-first-order and pseudo-second-order models are expressed as Eq. (5) and Eq. (6) [26];

$$\ln(q_e - q_t) = \ln(q_e) - \frac{k_1 t}{2.303} \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where q_e and q_t are the amount of Pb(II), Fe(II) and Cu(II) adsorbed (mg/g) at equilibrium and time t (min); k_1 is the rate constant of pseudo-first-order (min^{-1}); k_2 is the rate constant of pseudo-second-order ($\text{g mg}^{-1} \text{min}^{-1}$) for adsorption.

The results of the kinetic parameters are listed in Table 2. The correlation coefficient values by the straight-line plot of t/q_t against t of the pseudo-second-order kinetics model were much higher than for the pseudo-first-order kinetics model. These results indicated that the kinetics of Pb(II), Fe(II) and Cu(II) ions adsorption onto CS best fit the pseudo-second-order model (Figure 7).

CONCLUSION

The present study focuses on adsorption of Pb(II), Fe(II) and Cu(II) from aqueous solution using the CS as an effective adsorbent. The results of adsorption experiments revealed that the removal efficiency of the CS is strongly affected by the initial solution pH. The optimum pH for the maximum adsorption by CS were found at pH 6.0, 5.0 and 6.0 for Pb(II), Fe(II) and Cu(II), respectively. Moreover, increases in the initial metal concentrations from 100 to 1000 mg L^{-1} , led to reduction in adsorption ratio of Pb(II), Fe(II) and Cu(II) ions by CS. Adsorption equilibriums were attained after 60, 40 and 60 min for Pb(II), Fe(II) and Cu(II), respectively. The adsorption efficiency of Pb(II), Fe(II) and Cu(II) on CS increases with increasing adsorbent dose. Isotherm modeling revealed that the Langmuir equation could better describe the adsorption of Pb(II), Fe(II) and Cu(II) ions on the CS as compared to Freundlich model and kinetic of adsorption process follow second order kinetic model. Finally, CS shows great

potential as an effective, low-cost alternative material for metals removal from aqueous solution.

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