

Equilibrium Adsorption and Kinetics Studies on Removal of Chromium and Copper onto Chitosan-g-Maleic Anhydride-g-Styrene

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The present work was designed to remove chromium and copper using the double grafted copolymer chitosan-g-maleic anhydride-g-styrene. Ceric ammonium nitrate was used as an initiator for the preparation of graft copolymer. Prepared chitosan-g-maleic anhydride-g-styrene was used in order to remove the chromium and copper from aqueous solutions of 200 ppm/L concentration proceeding batch adsorption process by varying the parameters such as pH, contact time, adsorbent dose and initial concentration of the metal solution. The experimental data were equipped with Langmuir and Freundlich isotherm models and pseudo-first order and pseudo-second order kinetics. The calculated results suggested that the adsorption favours Freundlich isotherm following pseudo-second order kinetics.

Keywords: Graft polymerization, Chitosan-g-maleic anhydride, Styrene, Adsorption.

INTRODUCTION

Water pollution is primarily caused by the effluent prominently from leather and chemical industries, electroplating industries and dye industries [1]. The polluted water may contain many contaminant, among them, heavy metals are the most important for their non-degradable nature and often accumulate in an ecosystem, causing an adverse biological effect. Therefore, heavy metal pollution becomes an invasive and extremely serious environmental problem all over the world. It was pointed out that over 3 million sites in the United States, including municipal and industrial landfills, require remediation at a cost ranging from 250 billion to 1 trillion dollars [2]. Comparing with the developed countries, many developing countries are even more seriously affected by heavy metal pollution because of their low environmental consciousness and their desire for excess economic benefits [3]. Hence, the proper management of the global environment is increasingly growing up to be an essential issue. The metal ions like mercury and cadmium are highly toxic even in lower concentration than other metals [4,5].

To get rid these toxic heavy metals, various methods have been adopted which includes the precipitation, reduction, ion exchange, *etc.* But these methods are expensive and inefficient in handling large quantities, also they cause metal bearing sludges which are difficult to dispose off. Due to this, there is

just an increasing demand for the newer method which can effectively remove the toxic metals in a cost effective way. Now-a-days, biosorption is being a feasible option over conventional treatment methods because it incorporates a low cost, high efficiency removal even from dilute solution, minimization of sludge, no additional nutrient requirement and regeneration of biosorbent and the possibility of metal recovery. The biosorption process uses the natural polymers as the biosorbents. Since there are many low cost adsorbents, chitosan is one among them which have attracted significant attention lately.

Chitosan is a high molecular weight heteropolymer with high content of amine (NH₂) functional group composed mainly of β-(1,4)-linked D-glucosamine and partially of β-(1,4)-linked N-acetyl-D-glucosamine (Fig. 1). Chitosan is a unique basic polysaccharide which was obtained from chitin after alkaline deacetylation [6]. It is soluble in dilute acids. Chitosan is the only pseudo-natural cationic polymer and finds more applications in various subject areas especially in the wastewater treatment.

During the wastewater treatment process the reactive amine groups present in chitosan interact with metal ions by chelation or electrostatic force of attraction depending up on the pH of the metal solution and total metal ion composition. Though chitosan is the most promising material, its poor solubility, low surface area and porosity limits its use. Therefore

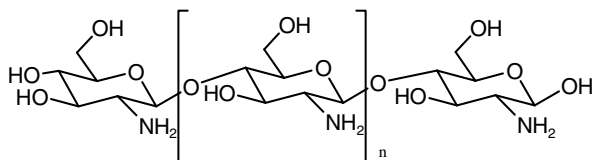


Fig. 1. Structure of chitosan

for maximum utilization of chitosan, it can be modified through physical or chemical processes in order to improve its physico-chemical properties for further diversify its applications. The modification strategies which have been adopted includes cross-linking [7,8], graft copolymerization [9,10], complexation [11], blending [12] and composite formation. Of all modifications, graft copolymerization of monomer onto a polymer is quite a promising method for developing sophisticated functions, which enable a wide variety of molecular designs to afford novel types of tailored hybrid materials composed of natural polysaccharides and synthetic polymers [13].

Therefore to study the removal efficiency of the graft copolymer, the batch adsorption study was conducted with novel synthesized chitosan-*g*-maleic anhydride-*g*-(styrene) graft copolymer. The adsorption parameters such as pH, contact time, adsorbent dose and initial metal ion concentration was subjected in treating chromium and copper containing aqueous solution to study its removal efficiency.

EXPERIMENTAL

Chitosan (92 % deacetylated) was purchased from India Sea Foods, Cochin, India. Ceric ammonium nitrate (CAN) and other chemicals used in the experiments were of analytical grade.

Preparation of chitosan-*g*-maleic anhydride copolymer:

The single graft copolymer of chitosan was prepared by mixing 2 g of chitosan and 5 g maleic anhydride dissolved in 100 mL of acetic acid under constant stirring at 70 °C. To this 10 mL of ceric ammonium nitrate (0.5 g ceric ammonium nitrate dissolved in 10 mL of nitric acid) was added and the stirring was continued for about 3 h under nitrogen atmosphere. After the completion of reaction the solution was cooled to room temperature and then poured into alkaline solution (10 % of NaOH) to precipitate the product. The precipitate formed was then collected by filtration, washed with diethyl ether for three times and then dried in vacuum at 40 °C. The grayish white powder of N-maleiated chitosan was obtained.

Preparation of chitosan-*g*-maleic anhydride-*g*-styrene copolymer: The double graft co-polymer of chitosan-*g*-maleic anhydride-*g*-styrene was synthesized by stirring the mixture of 0.5 g maleiated chitosan dissolved in 150 mL formic acid, 2 g of styrene dissolved in ethanol and 10 mL of ceric ammonium nitrate solution. The reaction temperature of about 70 °C and 30 min stirring was maintained to carry over the grafting reaction. After completion the mixture was cooled to room temperature and poured into 10 % NaOH solution to precipitate the graft co-polymer.

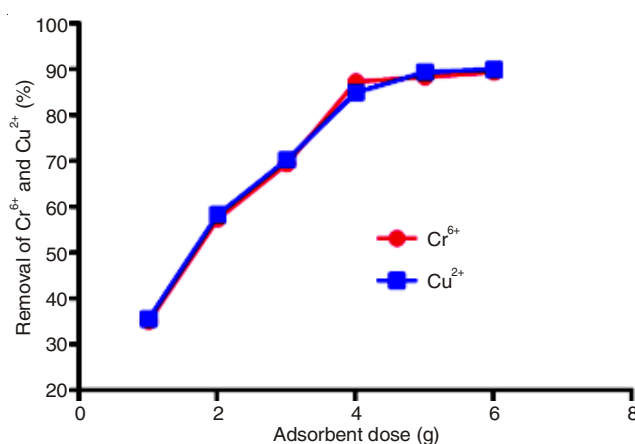
Adsorption studies of chromium and copper using the graft copolymers: At the optimum conditions of adsorbent dose and pH, the corresponding metal solutions of different initial concentrations were agitated and the liquid was taken

from the bottle to analyze the amount of un-adsorbed lead and chromium. The values were fitted into Freundlich and Langmuir adsorption isotherms and adsorption kinetics were studied.

RESULTS AND DISCUSSION

The removal of metal ions (chromium and copper) from metal solutions was carried out using chitosan-*g*-maleic anhydride-*g*-styrene by batch adsorption studies. The optimum conditions for the removal of toxic heavy metal ions was evaluated by varying the pH, adsorbent dose, contact time and initial metal ion concentration at constant temperature (30 °C).

Effect of adsorbent dosage: The effect of adsorbent dose on the removal of Cr(VI) and Cu(II) ions (Fig. 2) was studied by changing the adsorbent dose from 1 to 6 g by keeping the parameters such as pH 5.5 for Cr and 6.0 for Cu and contact time (60 min) as constant.

Fig. 2. Effect of adsorbent dose on the removal of Cr⁶⁺ and Cu²⁺

The removal efficiency for chromium was increased from 35.2 to 89.6 % and for copper it was increased from 35.8 to 90.2 % with the variation in adsorbent dose from 1 to 6 g. The gain in the percentage removal of chromium and copper to increase in amount of adsorbent dose was due to the availability of more adsorbent surfaces with active adsorption sites for the solutes to adsorb [14]. Among the two selected metals copper gets adsorbed more than chromium.

Effect of contact time: The effect of contact time (60-360 min) on the removal of chromium(VI) and copper(II) ion has been carried out with initial concentration of 200 mg/L at pH 5.5 for Cr and 6.0 for Cu. Fig. 3 shows the effect of contact time on adsorption of chromium(VI) and copper(II) ions. The results presented in Fig. 3 indicate that the metal removal for both Cr(VI) and Cu(II) was found to be the maximum at 360 min of time of contact. The rate of removal was rapid during the initial 240 min and thereafter the quickness of metal ion removal remains almost constant (*i.e.*) after some time further increase in contact time did not increase the uptake of heavy metals. This was due to the fact that large numbers of vacant active sites were available for adsorption during the initial adsorption process stage and hence it established a higher removal percentage, only after some time, due to repulsive forces between the solute molecules on the firm surface and bulk form, the remaining sites become difficult to occupy [15].

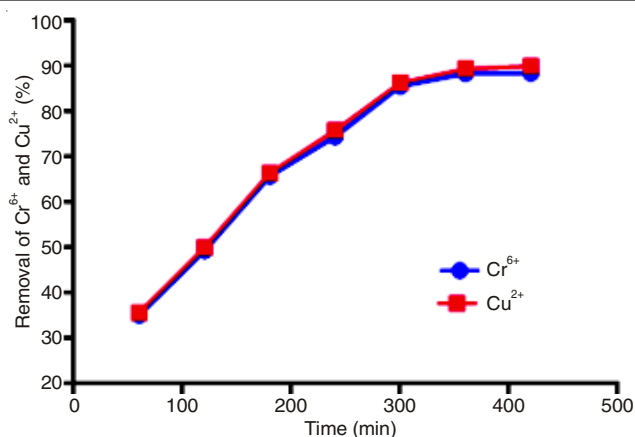


Fig. 3. Effect of time on the removal of Cr⁶⁺ and Cu²⁺

Effect of pH: The extent of removal of Cr(VI) and Cu(II) was investigated by varying the pH from 4 to 8 and the results are depicted in Fig. 4. It was observed that pH significantly affects the adsorption process of both the metals. The maximum adsorption was obtained at pH 5.5 for chromium and pH 6 for copper and after that adsorption decreased. This was due to the fact that at low pH, there was competition between H⁺ ions and metal ions for the binding site, resulted in the decrease in metal ions binding and when the pH value was higher than 5.5 for chromium and pH 6 for copper, heavy metal ions got precipitated leading to the reduction of the metal ions [16]. The adsorption process under different pH could be executed along the basis of surface charge density of the adsorbent and other working groups such as hydroxyl, carboxyl, amino and others face at the surface the copolymer.

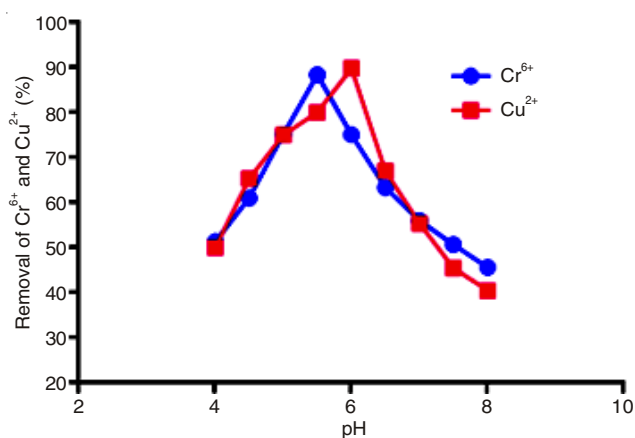


Fig. 4. Effect of pH on the removal of Cr⁶⁺ and Cu²⁺

Adsorption isotherm: The adsorption isotherms of Cr⁶⁺ and Cu²⁺ ions onto chitosan-g-maleic anhydride-g-styrene were plotted from determined and calculated parameters. Adsorption isotherms give the relationship between adsorption capacity and concentration of the remaining adsorbate at constant temperature. In this study, equilibrium sorption data were fitted into Langmuir and Freundlich isotherm equations.

Langmuir isotherm: The Langmuir equation has been frequently used to give the sorption equilibrium. The linearized form of Langmuir equation was used in the adsorption of Cr(VI) and Cu(II) by using chitosan-g-maleic anhydride-g-styrene and the results were presented below.

The linearized form of the Langmuir isotherm equation is expressed as follows:

$$C_{eq}/C_{ads} = bC_{eq}/K_L + 1/K_L$$

$$C_{max} = K_L/b$$

where, C_{ads} is the amount of metal ion adsorbed (mg g^{-1}); C_{eq} is the equilibrium concentration of remaining heavy metal ion in solution (mg dm^{-3}); K_L is the Langmuir constant ($\text{dm}^3 \text{g}^{-1}$); b is the Langmuir constant ($\text{dm}^3 \text{mg}^{-1}$) and C_{max} is the maximum metal ion to adsorb onto 1 g adsorbent (mg g^{-1}) corresponding to the saturation capacity of biosorbent.

The correlation coefficient R^2 , K_L and b (Table-1) were evaluated from the slope and intercept of the linear plot of C_{eq}/C_{ads} against C_{eq} (Fig. 5a and 5b). Dissociation constant represents the metal concentration matching to half-saturation of sorbent. Low values of b are reflected in the steep initial slope of sorption isotherm, indicating a desirable high affinity.

TABLE-1
ADSORPTION ISOTHERM CONSTANT, C_{max}
AND CORRELATION COEFFICIENT

Metal ion	Langmuir constants			R^2
	K_L (dm^3/g)	b (dm^3/mg)	C_{max} (mg/g)	
Cr(VI)	1.1579	0.01254	92.34	0.8110
Cu(II)	2.0333	0.02257	90.09	0.8963

The results of the adsorption isotherm in Table-1 showed a good correlation by the graft copolymer. The C_{max} value was 92.34 mg g^{-1} for chromium and for copper it was 90.09 mg g^{-1} . Correlation factor R^2 for chromium was 0.8110 and for copper it was 0.8963. From the results it was seen that Langmuir model fit well for Cu(II) than Cr(VI).

The values of R_L (Table-2) were calculated for different initial Cr(VI) and Cu(II) ions concentrations using chitosan-g-maleic anhydride-g-styrene. Since the calculated R_L values are obtained in the range of $0 < R_L < 1$, it was concluded that the adsorption of Cr(VI) and Cu(II) ions is favourable.

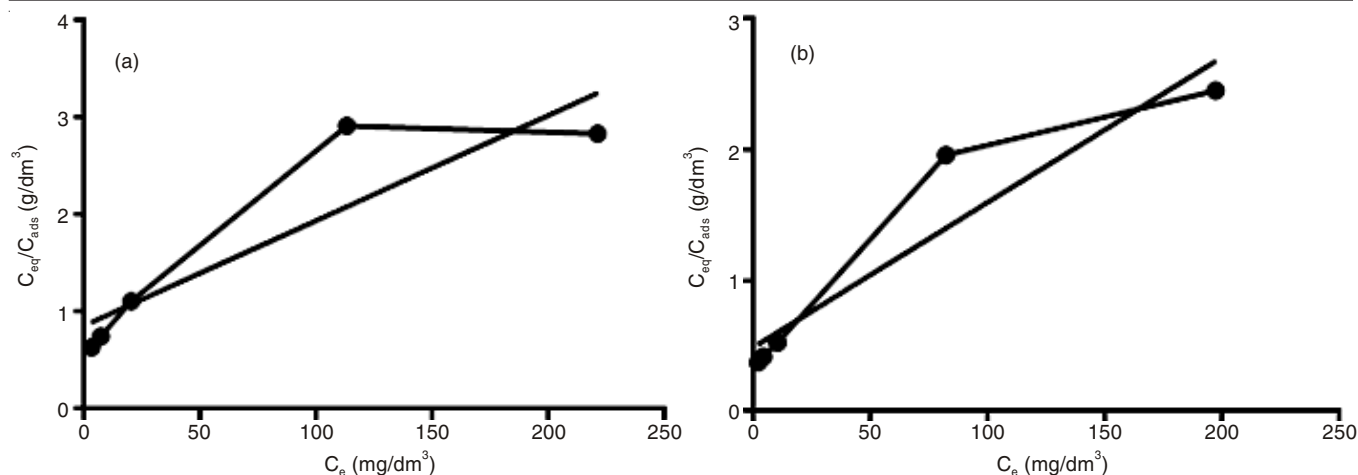
TABLE-2
 R_L VALUES BASED ON LANGMUIR ADSORPTION

Metal ions	Initial concentration C_0 (mg dm^{-3})	Final concentration C_f (mg dm^{-3})	R_L values
Cr(VI)	1000	779	0.0931
	500	387	0.1462
	200	194	0.2919
	100	95	0.4571
	50	45	0.6400
Cu(II)	1000	778	0.0540
	500	388	0.1027
	200	195	0.1856
	100	96	0.3164
	50	48	0.4807

Freundlich adsorption isotherm: The Freundlich isotherm equation is used to describe multilayer adsorption with the interaction between adsorbed molecules. This empirical equation takes the form:

$$q_e = K_F C_e^{1/n}$$

where, q_e = solid phase metal concentration (mg/g); K_F = related to adsorbent capacity; $1/n$ = "heterogeneity factor" ranging from 0 to 1; C_e = bulk liquid phase metal concentration.

Fig. 5. Langmuir isotherm for (a) Cr^{6+} and (b) Cu^{2+}

This can be linearized by taking the natural logarithm of both sides of the equation to give:

$$\log q_e = \log K_F + 1/n \log C_e$$

The intercept $\log K_F$ gives a measure of the adsorbent capacity and the slope $1/n$ gives the intensity of adsorption. The correlation coefficient R^2 , K_F and $1/n$ were calculated from the slope and intercept of the plot of $\log q_e$ versus $\log C_e$ (Fig. 6a and 6b). The magnitude of the Freundlich parameters K_F gives the quantitative information on the relative adsorption affinity towards the adsorbed cation and the magnitude of constant $1/n$ provide the information about the intensity of adsorption or surface heterogeneity [17].

The calculated values of Freundlich constants, correlation coefficient and heterogeneity coefficient was shown in Table-3. The Freundlich constants K_F values were 2.6303 for Cr^{6+} and 4.1543 for Cu^{2+} and n values were 1.6420 for Cr^{6+} and 1.7960 for Cu^{2+} . The Freundlich equation is appropriate for a highly heterogeneous surface and the R^2 values shows that an adsorption process follows multilayer adsorption. Since, $1/n < 1$ and “ n ” value lies between 1 and 10, represents beneficial adsorption.

In the present study both Langmuir and Freundlich model were discussed. According to regression coefficient the physical adsorption (Freundlich adsorption isotherm) was

TABLE-3 FREUNDLICH ISOTHERM PARAMETERS FOR $\text{Cr}(\text{VI})$ AND $\text{Cu}(\text{II})$ ON GRAFT COPOLYMER			
Metal ion	Freundlich constants		
	K_F (dm^3/g)	n (dm^3/mg)	R^2
$\text{Cr}(\text{VI})$	2.6303	1.6420	0.9859
$\text{Cu}(\text{II})$	4.1543	1.7960	0.9773

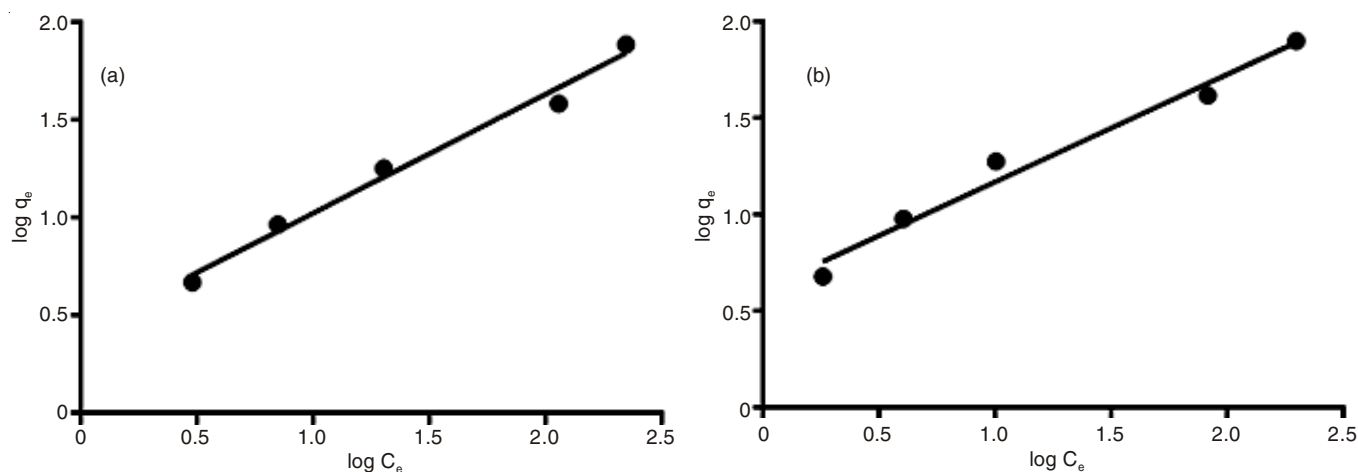
better fitted than the Langmuir. Hence the graft co-polymer Chitosan-*g*-maleic anhydride-*g*-styrene acts as a good adsorbent and can be used for wastewater treatment.

Kinetics of adsorption: When both physical and chemical adsorption is dominant then the pseudo-first order and pseudo second order models have been developed to fit experimental data [18]. This information is useful in the treatment of natural water and waste effluents.

Pseudo first-order kinetics: The first-order kinetic model was given as [19]:

$$\log (q_e/q_t) = \log q_e - k_1/2.303 * t$$

where, q_e = amounts of $\text{Cr}(\text{VI})$ and $\text{Cu}(\text{II})$ adsorbed on adsorbent (mg/g) at equilibrium; q_t = amounts of $\text{Cr}(\text{VI})$ and $\text{Cu}(\text{II})$ adsorbed on adsorbent (mg/g) at time t ; k_1 = rate constant of first-order adsorption (min^{-1}).

Fig. 6. Freundlich isotherm for (a) Cr^{6+} and (b) Cu^{2+}

The straight-line plots of $\log (q_e/q_t)$ against t were used to determine the rate constant, k_1 and correlation coefficient, R values of the Cr(VI) and Cu(II) under different concentration range were calculated from these plots. The pseudo first-order adsorption kinetic plot of chromium(VI) and copper(II) was represented in Fig. 7a and 7b.

Pseudo-second order kinetic model: The second-order equation may be expressed as Sag and Aytay [20]:

$$t/q_t = 1/k_2q_e^2 + t/q_e$$

where k_2 = the rate constant of second-order adsorption ($\text{g}/\text{mg}/\text{min}$)⁻¹.

The straight-line plots of t/q_t against t have been tested to obtain rate parameters and it suggests the applicability of this kinetic model to fit the experimental data (Fig. 8a and 8b).

From the above results pseudo first-order, pseudo second-order rate constant values presented in Table-4, it was identified

that the plot t/q_t vs. t for pseudo second-order model yields very good straight lines [correlation coefficient, $R^2 = 0.9861$ for Cr(VI) and $R^2 = 0.9878$ for Cu(II)] when compared to the plot of $\log (q_e/q_t)$ vs. t for pseudo first-order.

The obtained results reveal that the pseudo second order kinetics was followed when compared to the pseudo first order kinetics. The above fact suggests that the adsorption of Cr(VI) and Cu(II) ions by chitosan-g-maleic anhydride-g-styrene followed the pseudo second-order kinetic model (*i.e.*) chemisorptions may be rate-limiting [20].

Conclusion

This study appends to the increasing interest in the exposure of removal of Cr⁶⁺ and Cu²⁺ from water bodies contaminated with toxic heavy metals. The use of low cost adsorbent material and the enhanced sorption process of chromium and copper ions by chitosan-g-maleic anhydride-g-styrene are described

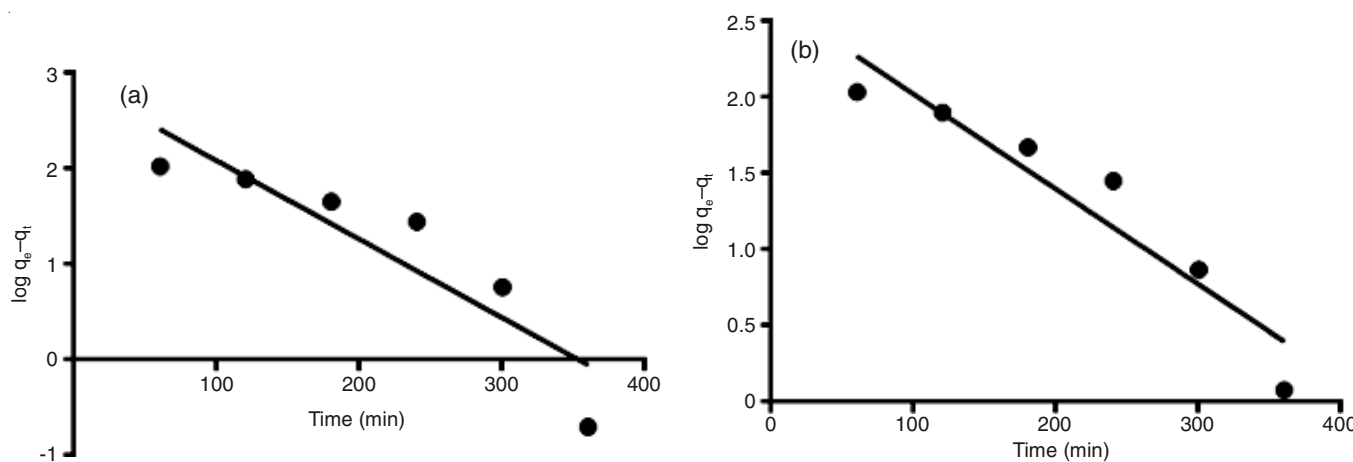


Fig. 7. Pseudo first-order sorption kinetic plot of (a) Cr⁶⁺ and (b) Cu²⁺

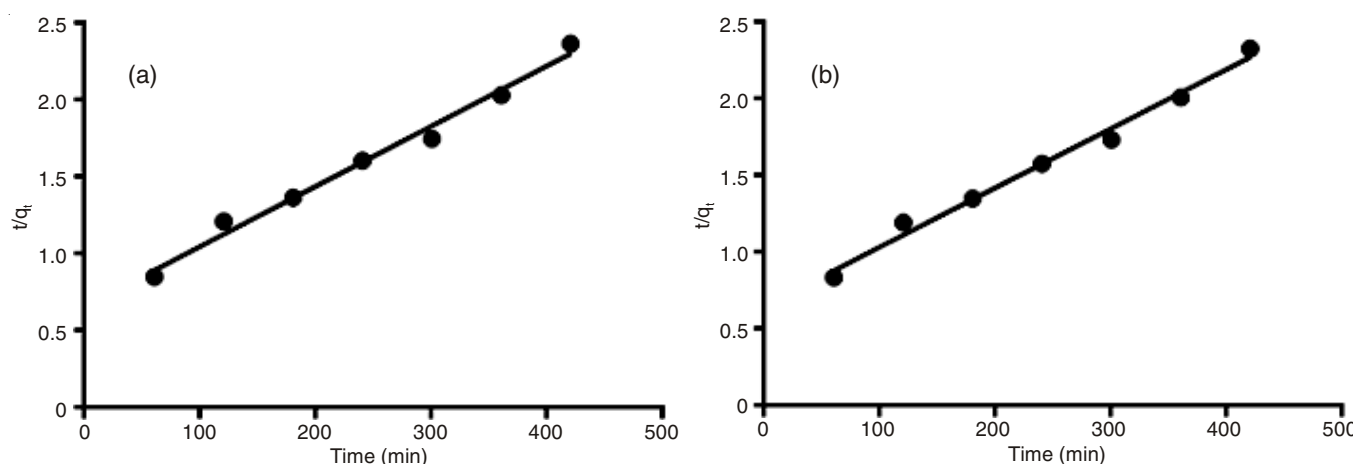


Fig. 8. Pseudo-second order sorption kinetic plot of (a) Cr⁶⁺ and (b) Cu²⁺

TABLE-4 COMPARISON BETWEEN LAGERGREN PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER KINETIC MODELS FOR Cr(VI) AND Cu(II) SORPTION BY CHITOSAN-g-MALEIC ANHYDRIDE-g-STYRENE							
Metal ion	Pseudo-first-order kinetic model			Experimental value q _e (mg/g)	Pseudo-second-order kinetic model		
	q _e (mg/g)	k ₁ (min ⁻¹)	R ²		q _e (mg/g)	k ₂ (g mg ⁻¹ min ⁻¹)	R ²
Cr(VI)	353.92	0.008211	0.8113	188	168.73	0.003914	0.9861
Cu(II)	423.97	0.006241	0.8965	192	168.67	0.003862	0.9878

in this study. The removal process was found to be dependent on pH of the solution, initial metal ions concentration, contact time and adsorbent dosage. The equilibrium data were fitted into Langmuir and Freundlich models. Freundlich isotherms gave a better fit for adsorption of both chromium and copper on to chitosan-*g*-maleic anhydride-*g*-styrene. The results of kinetics studies proved that the adsorption process follows pseudo-second-order kinetics. The process herein, is cost effective and attractive, which might help to reduce the disposal problems and thereby can also be used for heavy metal removal from aqueous systems as well as industrial effluent.

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