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Sorption studies of Cr (VI) from aqueous solution using nanochitosan-carboxymethyl cellulose blend

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ABSTRACT

The removal of Cr(VI) ions from aqueous solutions has been investigated using nanochitosan(NC)/carboxymethyl cellulose(CMC) blend under different experimental conditions of initial chromium concentration, adsorbent dose and pH. The adsorption data have been explained in terms of Langmuir and Freundlich equations. The sorption kinetics was tested for the pseudo-first order and pseudo-second order reaction. The results revealed that the adsorptions of Cr(VI) onto NC/CMC blend, was found to fit well with the Freundlich isotherm. The rate constants of sorption for kinetic models were calculated and good correlation coefficients obtained for the pseudo-second-order kinetic model. The results indicate that under the optimum conditions, the NC/CMC blend was found as an effective adsorbent for chromium.

Key words: Nanochitosan, Carboxymethyl cellulose blend, Chromium, Adsorption, Kinetics.

INTRODUCTION

Elemental chromium (Cr) does not occur in nature, but is present in ores, primarily chromite (FeOCr₂O₃) [1]. Chromium (Cr) was first discovered in the Siberian red lead ore (crocoite) in 1798 by the French chemist Vauquelin. It is a transition element located in the group VI-B of the periodic table with a ground-state electronic configuration of {Ar} 3d⁵4s¹. Chromium is a toxic metal of widespread use in many industries such as plating facilities, mining operations and tanneries [2]. Cr (III) and Cr (VI) are the species usually encounter in the environment. Chromium enters the air, water, and soil mostly in the chromium (III) and chromium (VI) forms. Chromium (III) is an essential nutrient that helps the body to use sugar, protein, and fat. Cr (III) is a very stable oxidation state for chromium. In this state, the chrome is labile and kinetically very slow to react or form complexes. It is not a strong oxidiser and the human's natural body acidity is enough for the chrome to keep to this Cr (III) state. Animal studies show that Cr (VI) is generally more toxic than Cr (III). In long-term studies, rats were not adversely affected by ~1.9

g/kg/day of chromic oxide [Cr (III)] (diet), 2.4 mg/kg/day of Cr (III) as chromic chloride (drinking water), or 2.4 mg/kg/day of Cr (VI) as potassium dichromate (drinking water) [3, 4]. Breathing high levels of chromium (VI) can cause irritation to the nose, such as runny nose, nosebleeds, and ulcers and holes in the nasal septum [5, 6, 7].

Ingesting large amounts of chromium (VI) can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death. Skin contact with certain chromium (VI) compounds can cause skin ulcers. Some people are extremely sensitive to chromium (VI) or chromium (III). Allergic reactions consisting of severe redness and swelling of the skin have been noted. The Cr (VI) is a very strong oxidizing agent (therefore very fast in reacting, unlike Cr (III) and likely to form complexes). The hexavalent form is of particular concern because of its greater toxicity [8]. Hence, the removal of Cr (VI) from industrial effluents is important. A conventional method for removing metals from industrial effluents includes chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion – exchange and adsorption. Most of these methods suffer with high capital and regeneration costs of the materials [9]. Therefore, there is currently a need for new, innovative and cost effective methods for the removal of toxic substances from wastewaters. Biosorption is an effective and versatile method and can be easily adopted in low cost to remove heavy metals from large amount of industrial wastewaters.

Chitosan is a natural material with excellent physicochemical properties. It is environmentally friendly and bioactive. It is frequently used as a controlled-release drug carrier for gene transfer in artificial organs and for immune prophylaxis. In addition, nanochitosan has been used to improve the strength and washability of textiles and to confer anti-bacterial effects [10]. Nanochitosan can be prepared in several ways. Nanochitosan is initially prepared from chitosan particles using sodium sulphate as the precipitation agent [11]. The technique is improved and obtained 600–800 nm chitosan nanoparticles [12]. Nanochitosan is widely used as drug carrier whereas it is used only to a certain extent in the adsorption studies. Nanochitosan can also be prepared by crosslinking with sodium tripolyphosphate to get particles of 100 – 400nm size. Chitosan is a very good adsorbent and the surface area of chitosan can be increased by converting it into nanochitosan. The film forming property of chitosan is reduced upon crosslinking and nanochitosan exists as fine particles. To improve the film forming property nanochitosan can be blended with suitable polymers in the presence of crosslinkers such as glutaraldehyde.

Carboxymethyl cellulose (CMC), one of the most important derivatives of cellulose, is a typical anionic polysaccharide that has been widely used as a stabilizer in food [13, 14]. CMC is one of the natural water-soluble cellulose derivatives that have no harmful effects on human health. CMC is used as a highly effective additive to improve product and processing properties in fields of application varying from foodstuffs, cosmetics, and pharmaceuticals to products for the paper and textile industries [15].

In this study, we explored the potential of using NC/CMC binary blend as an adsorbent to remove Cr(VI) metal ion from aqueous solutions. The aim of this study was to explore the novel sorbent which has a high affinity for Cr(VI) ions and fully exploit its ability in a wide range of metal concentrations. Experiments were carried out as function of pH, adsorbent dosage and contact time. The equilibrium and kinetic studies of the adsorption process are evaluated. This

information will be useful for further applications for the system design in the treatment of practical water effluents.

MATERIALS AND METHODS

Materials

All chemicals used in the present study were of analytical reagent grade. Chitosan (from crab shells) was the gift from India Seafoods, Cochin, Kerala, Carboxymethyl cellulose (CMC) was purchased from Sigma Aldrich, India. Analytical grade potassium dichromate was purchased from S.D. Fine Chemicals, chromium (VI) ion source. Hydrochloric acid and sodium hydroxide were from Chemical Drug House Ltd., India. Millipore water was prepared in the laboratory by double distillation of deionised water in quartz distillation plant.

Preparation of nanochitosan (NC)/carboxy methyl cellulose (CMC) blend with Glutaraldehyde as crosslinking agent

10 g chitosan was dissolved in 2000 ml of 2.0 % (v/v) acetic acid. 100 ml of 0.75 mg/ml TPP was dropped into the beaker. Then the solution was filtered to remove the residual TPP. The nanochitosan was washed several times in water and freeze dried. About 10 grams of CMC was slowly added to 200 ml of water stirred well and allowed to dissolve.

The NC/CMC blends were prepared by mixing NC and CMC in the weight ratio 30:1 and 10 ml of crosslinking agent glutaraldehyde was added with stirring for 2 hours.

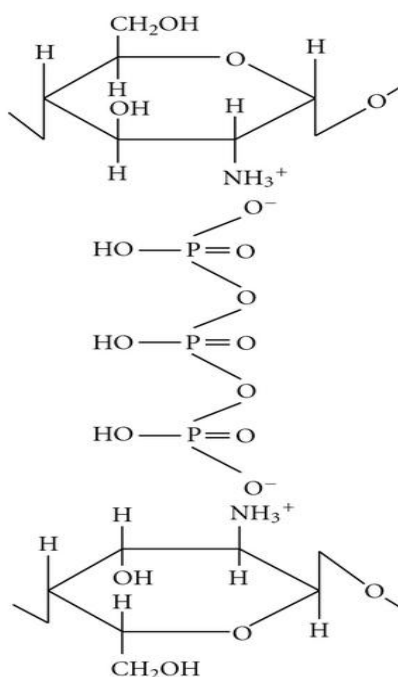


Figure 1. Structure of nanochitosan [16]

Formation of nanochitosan was proved by Scanning Electron Microscopy studies using SEM analyzer (JSM 6400; Joel. Tokyo, Japan) studies. Particle size distribution was analysed using Nanotracs 150 particle size analyzer which works based on dynamic light scattering.

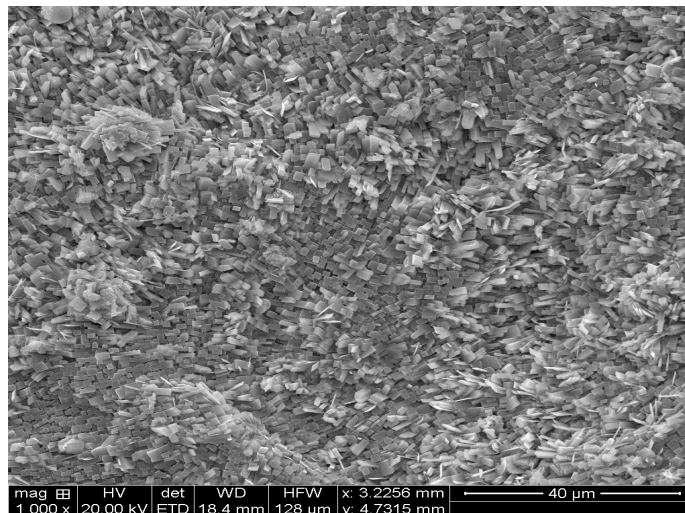


Figure – 2: SEM image of nanochitosan

Preparation of potassium dichromate solution

The stock solutions of Cr(IV) was prepared to get a concentration of 200mg/L of chromium as potassium dichromate. 1:1 Hydrochloric acid and 2N sodium hydroxide solutions were used for pH adjustment. The exact concentration of each metal ion solution was calculated on mass basis and expressed in terms of mg L^{-1} . The required lower concentrations were prepared by dilution of the stock solution. All precautions were taken to minimize the loss due to evaporation during the preparation of solutions and subsequent measurements. The stock solutions were prepared fresh for each experiment as the concentration of the stock solution may change on long standing.

Experimental

Batch studies were performed with different concentrations of potassium dichromate to investigate the extent of adsorption. Synthetic solution of Cr(VI) ion taken in stoppered bottles and agitated with the blend films at 30°C in orbit shaker at fixed speed of 210rpm. The extent of heavy metal removal was investigated separately by changing adsorption dose, contact time and changing pH of the solution. After attaining the equilibrium adsorbent was separated by filtration using filter paper and aqueous phase concentration of metal was determined with atomic adsorption spectrophotometer (Varian AAA 220FS).

RESULTS AND DISCUSSION

SEM

Figure - 2 shows the SEM image of nanochitosan. The particles are having cubic to cuboid shape with 100-300nm particle size as given by Nanotracs particle analyzer. The prepared nanochitosan was blended with carboxymethyl cellulose in the ratio 30:1 in the presence of glutaraldehyde as crosslinking agent. The blend was analysed for its adsorptive ability of heavy

metal chromium in water. Conditions such as adsorbent dose, contact time and pH of the medium were changed and the adsorption rate was studied.

Effect of Adsorbent Dose

The effect of the adsorbent dosage on the chromium adsorption on nanochitosan/carboxymethyl cellulose binary blend in the presence of glutaraldehyde as crosslinking agent is shown in Figure - 3. The % removal of chromium increased with the increase of the adsorbent dosage. The increase in adsorption with the increase in amount of adsorbent (NC/CMC binary blend) dose may be attributed to the fact that more surface area is available for adsorption to occur. The number of available adsorption sites increases by increasing the sorbent and it results an increase in removal efficiency. It can be concluded that by increasing the adsorbent dose, the removal efficiency increases.

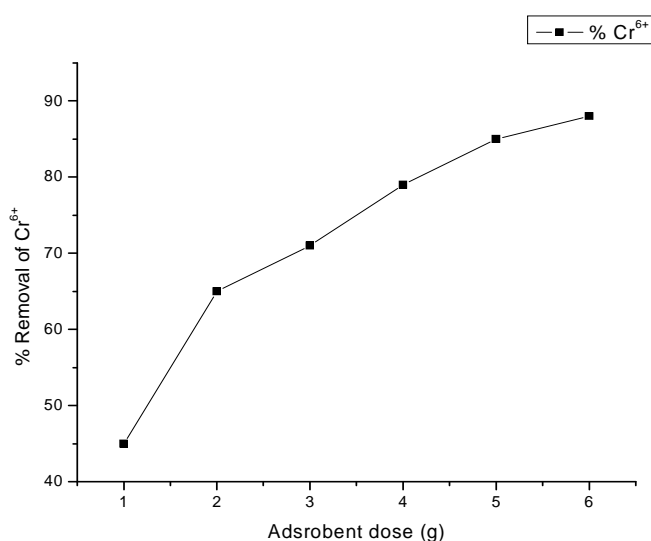


Figure 3: Percentage removal of chromium ion using nanochitosan/carboxymethyl cellulose blend at different adsorbent dose

Effect of pH

The role of hydrogen ion concentration was examined in solutions at different pH [17]. The pH of the solution affects the surface charge of the adsorbents [18]. The hydrogen and hydroxyl ions are adsorbed quite strongly, and therefore the adsorption of other ions is affected by the pH of the solution [19]. It was observed that with the increase in the pH of the solution, the extent of metal ions removal increased for the adsorbent. The maximum adsorption was obtained at pH 5. The concept of increasing metal removal with increasing pH can be explained on the basis of a decrease in competition between proton and metal cations for same functional groups and by the decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions. Decrease in adsorption at higher pH is due to formation of soluble hydroxyl complexes.

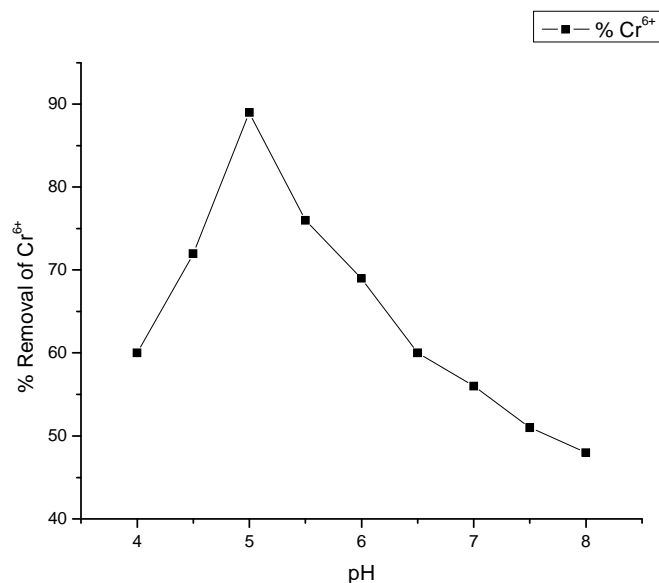


Figure 4: Percentage removal of chromium ion using nanochitosan/carboxymethyl cellulose blend at different pH

Effect of contact time:

Efficient uptake of the Chromium ion with the effect of contact time by the NC/CMC binary blend was studied and the results are shown in Figure - 5. The efficiency increases with increase in time of contact, due to the availability of more time for metal ions to make an attractive complex with the composite. Initial removal occurs immediately as soon as the metal and composite came into contact and after some extent further increase in contact time did not increase the uptake due to decrease of the easily available active sites for the binding of metal ions, the equilibrium is reached. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

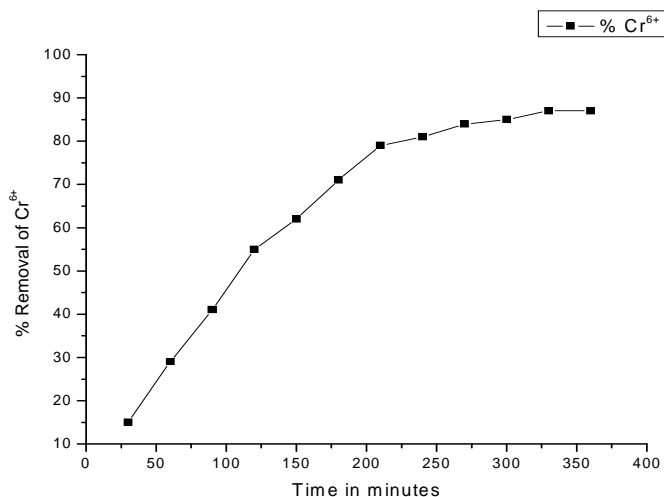


Figure 5: Percentage removal of chromium ion using nanochitosan/carboxymethyl cellulose blend at different time intervals

Adsorption studies

Sorption kinetics is an important physicochemical parameter to evaluate the basic qualities of a good sorbent (such as whether or not the sorbent adsorbs metals). Removal of Cr (VI) by nanochitosan/carboxymethyl cellulose blend as a function of time at pH 5, at various initial Cr (VI) concentrations, is shown in Fig. 6. The results indicate that as the concentration of the Cr (VI) is increased, so does the time taken before equilibrium is reached. It also appears that at lower concentrations less Cr (VI) adsorbs onto the blend than at higher concentrations.

The Langmuir equation has been frequently used to give the sorption equilibrium [20]. The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions [21]. To get the equilibrium data, initial metal concentration were varied while the adsorbent mass in each sample was kept constant. The linearized Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constant by the following equation:

$$C_{ads} = (K_L C_{eq}) / (1 + b C_{eq}) \quad (1)$$

In this study the following linearised form of the Langmuir isotherm was used.

$$C_{eq}/C_{ads} = b C_{eq}/K_L + 1/K_L \quad (2)$$

And

$$C_{max} = K_L/b \quad (3)$$

where:

C_{ads} = amount of Cr (VI) adsorbed ($\text{mg}\cdot\text{g}^{-1}$)

C_{eq} = equilibrium concentration of Cr (VI) in solution ($\text{mg}\cdot\text{dm}^{-3}$)

K_L = Langmuir constant ($\text{dm}^3\cdot\text{g}^{-1}$)

b = Langmuir constant ($\text{dm}^3\cdot\text{mg}$)

C_{max} = maximum Cr (VI) to adsorb onto 1 g chitosan ($\text{mg}\cdot\text{g}^{-1}$)

The constant b in the Langmuir equation is related to the energy or the net enthalpy of the sorption process. The constant K_L can be used to determine the enthalpy of adsorption [22]. A plot of C_{eq}/C_{ads} vs C_{eq} confirming the applicability of the Langmuir adsorption isotherm.

Freundlich equation plot of $\log C_{ads}$ vs. $\log C_{eq}$ yielded a straighter line as shown in Fig.7. The linearity of the plot supports the applicability of the Freundlich adsorption isotherm in this study. The Freundlich equation which is used to describe heterogeneous surface energies, is expressed as:

$$C_{ads} = P C_{eq}^{1/n} \quad (4)$$

In this study the following linearised form of the Freundlich equation was used.

$$\log C_{ads} = \log P + 1/n \log C_{eq} \quad (5)$$

where:

C_{ads} = amount of Cu (II) adsorbed ($\text{mg}\cdot\text{g}^{-1}$)
 C_{eq} = equilibrium concentration in solution ($\text{mg}\cdot\text{dm}^{-3}$)
 $1/n$ = Freundlich constant ($\text{mg}\cdot\text{g}^{-1}$)
 P = Freundlich constant ($\text{g}\cdot\text{dm}^{-3}$)

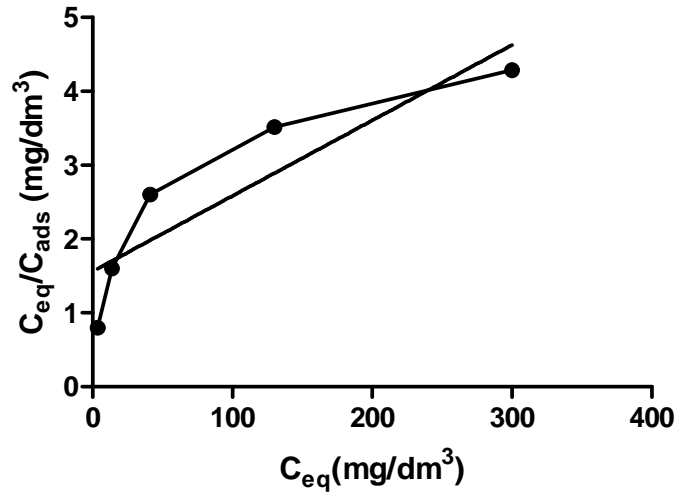


Figure 6 Langmuir plot for the adsorption of chromium ion onto nanochitosan/carboxy methyl cellulose blend

From Fig. 7 it is evident that the values of $1/n$ and P , which are rough measurements of the adsorption intensity and adsorption capacity of the adsorbent, have been determined by the least-square fit.

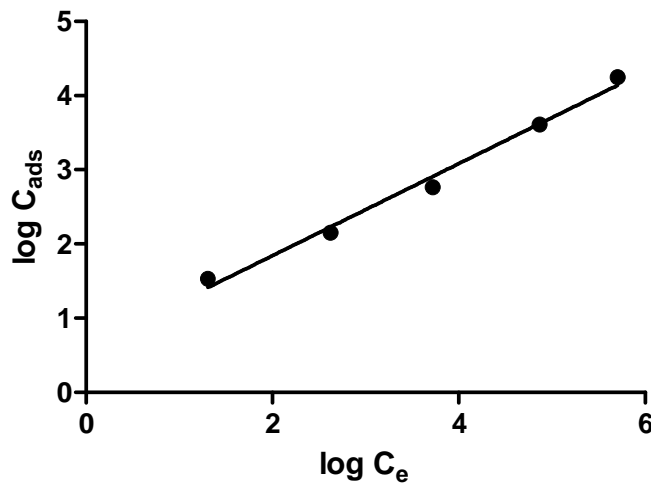


Figure 7 Freundlich plot for the adsorption of chromium ion onto nanochitosan/carboxy methyl cellulose blend

Analysis of equilibrium data is important for developing an equation that can be used to design and optimize an operating procedure. To examine the relationship between biosorption and aqueous concentration at equilibrium, various biosorption isotherm models are widely employed for fitting the data. The Freundlich isotherm is originally empirical in nature [23], but was later

interpreted as biosorption to heterogeneous surfaces or surfaces supporting sites of varied affinities and has been used widely to fit experimental data [24]. The value of n , of this model, falling in the range of 1– 10 indicates favourable biosorption [25].

Table 1: The Langmuir isotherm and Freundlich isotherm parameters of nanochitosan/carboxymethyl cellulose blend

Metal ions	Langmuir constants				Freundlich constants		
	K_L (dm ³ /g)	b (dm ³ /mg)	C_{max} (mg/g)	R^2	P	n	R^2
Cr(VI)	1.561	0.01022	152.74	0.8054	1.8247	1.6124	0.9889

The numerical value of $1/n < 1$ indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the adsorbent by the adsorbate. Thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface [26]. The present study results indicate that the Freundlich model fit the experimental data well. The adsorption data provided an excellent fit to the Langmuir isotherm. The separation factor (R_L) value indicates that Cr (VI) biosorption of biosorbent in this study is favourable. It can be seen from the table, *nanochitosan/carboxymethyl cellulose binary blend* used in this study has high biosorption capacity.

Kinetics studies

The kinetics of chromium biosorption on NC/CMC binary blend were analyzed using pseudo-first-order [27], Elovich [28] and pseudo-second-order [28] kinetics models. The linearized form of pseudo-first-order Lagergren equation is given as Eq. (6).

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

The pseudo-second-order rate equation is given as Eq. (7) [29]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where q_e and q_t are the amounts of metal adsorbed (mg/g) at equilibrium and at time t (min), k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the adsorption rate constant of pseudo-first-order, pseudo-second-order adsorption rate, respectively.

The linear plots of $\log (q_e - q_t)$ versus t and (t/q_t) versus t are drawn for the pseudo-first-order and the pseudo-second-order models, respectively. The rate constants k_1 and k_2 can be obtained from the plot of experimental data.

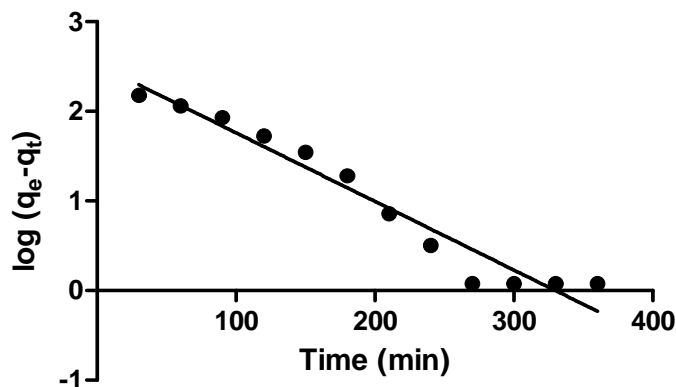


Figure 8: Pseudo-first-order for chromium adsorption by nanochitosan/carboxymethyl cellulose blend

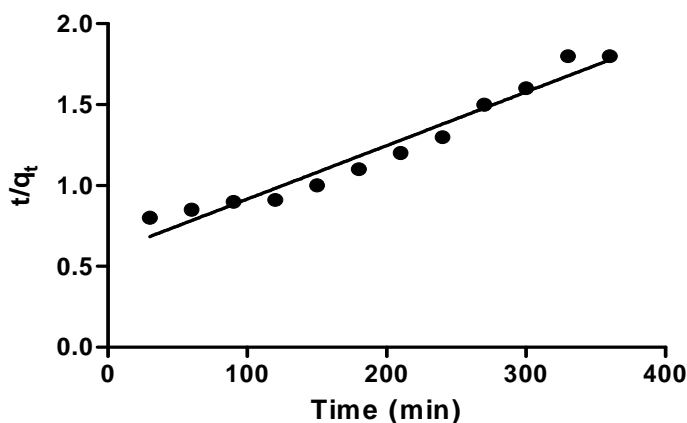


Figure 9: Pseudo-second-order for chromium adsorption by nanochitosan/carboxymethyl cellulose blend

Table 2 Comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models for NC/CMC binary blend

Metal ion	Pseudo-first-order kinetic model			Experimental value	Pseudo-second-order kinetic model		
	qe (mg/g)	k ₁ (min ⁻¹)	R ²	qe (mg/g)	qe (mg/g)	k ₂ (g mg ⁻¹ min ⁻¹)	R ²
Cr(VI)	330.07	0.007656	0.9509	185.2	176.59	0.003310	0.9555

The values of k_1 can be determined from the slope of the linear plot of $\log(q_e - q_t)$ versus t , and k_2 can be calculated from the slope of the linear plot t/q_t versus t . The linear plots of two kinetic models are presented in Figure 8 and Figure 9, respectively. The values of k_1 , k_2 , q_e and the correlation coefficient (R^2) from the linear plots are shown in Table 2. The pseudo-second-order linear plots resulted in higher R^2 values than the pseudo-first-order. The values of q_e (cal) from the pseudo-second-order were more close to q_e (exp) than that from the pseudo-first-order. These indicated the better applicability of the pseudo-second-order model.

CONCLUSION

The adsorption capacity of Chromium (VI) metal ion adsorbed onto the NC/CMC binary blend adsorbent was observed to be related to the solution pH, reaction time, and initial concentration

of chromium. The functional groups on the biosorbent surface were found to play a role in the entrapment of the target chromium ions. Since biosorbent used in this work is freely, abundantly, locally available, it is expected to be a viable adsorbent for removal of chromium ion from aqueous solution. Results obtained were modeled using Langmuir and Freundlich isotherms. The equilibrium data were well fitted with a Freundlich isotherm equation according to the nonlinear curve fitting regressive analysis, indicating that multilayer maximum adsorption capacity of chromium onto NC/CMC binary blend. The kinetic study of chromium adsorption onto the NC/CMC binary blend adsorbent revealed that the pseudo-second order model yields a much better fit than the pseudo-first order model.

REFERENCES

- [1] J.W. Hamilton, and K.E. Wetterhahn, Chromium In: Handbook on Toxicity of Inorganic compounds, Seiler, H.G. and Sigel Eds., Marcel Dekker, New York, **1988**, pp239.
- [2] N. Fiol, I. Villaescusa, M. Martinez, N. Miralles, J. Poch, and J. Serarols, *Environ. Chem. Lett.*, **2003**, 1, pp135-139.
- [3] S. Ivankovic, R. Preussmann, *Food Cosmet. Toxicol.* **1975**, **13**, pp347-351.
- [4] MacKenzie, R.D., Byerrum, R.U., Decker, C.F., Hoppert, C.A. and R.F. Langham, *Am. Med. Assoc. Arch. Ind. Health*, **1958**, 18, pp232-234.
- [5] RB. Hayes, *Rev Cancer Epidemiol.* **1980**, 1: pp293-333.
- [6] A. Leonard, and R.R. Lauwerys, *Mutat. Res.*, **1980**, 76: pp227-239.
- [7] S. Langard, Biological and environmental Aspects of Chromium. McGraw Hill Book Co., Inc., New York. **1893**, Pp.314.
- [8] C. Baird, & M. Cann, *Environmental Chemistry, third edition*. New York: W. H. Freeman and Company. **2005**.
- [9] C. P. Huang, and M. H. Wu, *J. Water. Pollut. Control Fed.*, **1975**, **47**, pp2437-2445.
- [10] D. R. Ting, and Y. Shen, *Dyeing and Finishing*, **2005**, 14, pp12-14.
- [11] A. Berthold, K. Cremer, and J. Kreuter, *Journal of Control Release*, **1996**, 39, pp17-25.
- [12] X. X. Tian, and M. J. Groves, *Journal of Pharmacy and Pharmacology*, **1999**, 51, pp151-157.
- [13] H. Togrul, and N. Arslan, *Journal of Food Engineering*, **2004a**, 62(3), pp271-279.
- [14] H. Togrul, and N. Arslan, *Food Hydrocolloids*, **2004b**, 18(2), pp215-226.
- [15] C. Schmitt, C. Sanchez, S. Desobry-Banon, and J. Hardy, *Critical Reviews in Food Science and Nutrition*, 1998, 38(8), pp689-753.
- [16] M.N. Rao, A.V. Parwate, and A.G. Bhole, *Waste management*, **2002**, 22: pp821-830.
- [17] D. P. Chattopadhyay, and S. Milind Inamdar, *International Journal of Polymer Science*. Volume **2010**, Article ID 939536, 7 pages
- [18] H. A. Elliott and C. P. Huang, *Water Res*, **1981**, 15, pp849-854
- [19] H. Yu, G.H. Covey, and A.J. O'Connor, *Appita Journal*, **2001**, Vol. 54, pp.511-517.
- [20] B. Koumanova, P. Peeva, S. J. Allen, K. A. Gallagher, and M. G. Healy, *Journal of Chemical Technology and Biotechnology*, **2002**, 77, pp 539-545.
- [21] I. Langmuir, *J Am Chem Soc*, **1916**, 38, pp2221-2295
- [22] R. Schmuhl, H.M. Krieg, K. Keizer, *WaterSA*, **2001**, 27(1), 1-83.
- [23] H. M. F. Freundlich, Uber die adsorption in losungen, *Zeitschrift fur Physikalische Chemie (Leipzig)*, **1906**, 57A pp385-470
- [24] Z. Aksu, and T. Kutsal, *J. Chem. Technol. Biotechnol.*, **1991**, **52**, 109- 118.

[25] Z. Aksu, *Proc. Bio.*, **2002**, 89-99.

[26] S.M. Hasany, M.M. Saeed, and M. Ahmed, *J. Radioanal. Nucl. Chem.*, **2002**, 252(3), pp477– 484

[27] Y.S. Ho, *Scientometrics*, **2004**, 59,171–177.

[28] Y. S. Ho, *J. Hazard Mater.*, **2006**, 136, 681–689

[29] Y.S. Ho, and G. McKay,). *Process Biochem.* **1999**, 34, pp451–465.