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Studies on removal of Cr(VI) and Cu(II) ions using Chitosan-grafted-polyacrylonitrile

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ABSTRACT

In the present work, graft copolymerization of polyacrylonitrile onto chitosan has been carried out in the presence of ceric ammonium nitrate redox initiator. Chitosan has been used as an adsorbent for the removal of heavy metal ions from aqueous solution through adsorption process. The property of chitosan is enhanced by grafting. The prepared copolymer was characterized by FTIR, XRD and SEM. The effect of pH, contact time and amount of adsorbent dose were also investigated. The adsorption kinetics of chitosan-g-polyacrylonitrile was found to follow pseudo-second-order kinetic model. The experimental data were fitted to Langmuir adsorption isotherms.

Key words: Chitosan-g-polyacrylonitrile, Adsorption isotherm, Kinetics model.

INTRODUCTION

Water is one of the essential items needed for living beings for the survival and growth. It also maintains an ecological balance between various groups of organisms and their environment [1]. Heavy metals are widely used in the industries like textiles, leather, paper, plastics, electroplating, cement, metal processing, wood preservatives, paints, pigments and steel fabricating industries [2]. These industries discharge large quantities of toxic wastes and the untreated effluents from these industries causes water pollution [3].

A wide range of physical and chemical processes are available for the removal of these metals from waste waters, such as precipitation, ultrafiltration, adsorption, ionexchange, reverse osmosis, oxidation, ozonation, coagulation, flocculation and membrane filtration processes [4]. Among these, adsorption techniques have been proved to be an excellent method to treat waste water, offering advantages over conventional processes [5]. It is now recognized that adsorption

using low cost-adsorbents is an effective and economic method for the removal of heavy metals in waste water. However, low- cost adsorbents with high adsorption capacities are still under development to reduce the adsorbent dose and minimize disposal problems.

Much attention has recently been focused on biopolymers as bioadsorbents. They are naturally produced by all living organisms. Bioadsorbents are a useful option since they have no adverse impact on human or environmental health. Polysaccharides such as chitosan a natural amino polymer plays a vital role in the treatment of waste water.

Chitosan is a unique basic polysaccharide and partially deacetylated polymer of glucosamine obtained after alkaline deacetylation of the chitin [6]. It consists of mainly of β -(1-4-2-acetamido-2-deoxy-D-glucose) units and is the second most abundant biopolymer on earth after cellulose, widely distributed in crustacean shells and cell walls of fungus [7,8]. Chitosan is soluble in dilute acids. The solubilisation occurs by the protonation of the $-NH_2$ function on the C-2 position of the D-glucosamine repeat unit, where by the polysaccharide is converted to a polyelectrolyte in acidic media. Chitosan is the only pseudo natural cationic polymer and thus it finds applications in the wastewater treatment. A few review articles on the potential applications of chitosan for pharmaceutical, veterinary medicine, and biomedicine are found in literature.

Chitin and chitosan are widely used for waste water treatments of polymers experimentally proven that decrease the chemical oxygen demand, total nitrogen and destroy the microbial population [9,10]. However, due to its low mechanical strength and flexible behaviour, chitosan has limited application of water treatment, while addition of synthetic polymers increased its properties tremendously. Besides these applications chitosan has few drawbacks such as acidic solubility, low thermal and mechanical stability. To improve these drawbacks, chitosan can be modified physically and also chemically. Now days, a lot of attention has been paid on chemical modification of chitosan. One such important modification is graft copolymerization [11-14]. Of all possible modifications, graft copolymerisation of vinly monomers onto natural polysaccharides [15,16] is quite promising.

Grafting onto chitosan and its derivatives has been the thrust of researchers. In Chitosan, both hydroxyl and amino groups are possible sites for the reaction to incorporate new and desired functional groups. Graft copolymerization of synthetic polymers onto chitosan can introduce desired properties and enlarge the field of the applications by choosing various types of side chains.

In recent years, a number of initiator systems such as APS, PPS, CAN, FAS have been developed to initiate graft copolymerization [11, 12, 17-20].

Many investigations have been carried out on the grafted copolymerization of chitosan and it is considered to be a promising approach for designing a wide variety of molecular matrices.

Graft copolymerization of acrylamide on chitosan using ammonium per sulfate as an initiator, was prepared. The effect of temperature, pH of the medium and concentrations of initiator, chitosan and acrylamide on grafting kinetics and efficiency were established. Graft copolymerization of mixtures of acrylic acid and acrylamide onto chitosan using potassium per

sulphate as initiator and methylenebisacrylamide as a cross-linker was carried [21]. Semi-interpenetrating polymer network hydrogel was prepared to recognize hemoglobin, by molecularly imprinted method, in mild aqueous media of chitosan and acrylamide in the presence of N,N'-methylenebisacrylamide as the cross linking agent [22].

In the present study, chitosan has been graft copolymerized with acrylonitrile with an aim to develop a product, which could be used for wastewater treatment. The effect of reaction conditions on grafting parameters has been studied to obtain the product and the properties of the graft copolymer have been studied. The obtained copolymer was subjected to various analytical techniques such as FTIR, DSC, TGA, XRD and SEM to confirm the copolymer formation. Adsorption study was carried out as a function of pH, adsorbent dosage and contact time. From the results we have concluded that, the formation of copolymer of acrylonitrile on the chitosan matrix was in proper arrangement to remove heavy metals from waste water.

MATERIALS AND METHODS

Chemicals

Chitosan was received from India seafoods, Cochin, ceric ammonium nitrate, concentrated nitric acid and acrylonitrile were of analytical grade and used as received.

Instrumentation

pH meter (ELICO) was used for the adjustment of pH with HCl (0.1M) to decrease the pH and NaOH (0.1M) to increase. Absorbance of the standards and samples of chromium and copper were recorded on atomic absorption spectrophotometer (Varian AAA 220 FS).

Adsorbate Solution

Synthetic stock solutions of heavy metals were prepared by dissolving required quantity of analar grade salts in distilled demineralised water. Stock solution was further diluted with distilled demineralised water to desired concentration for obtaining test solutions.

Preparation of Adsorbent

A 2% w/v solution of chitosan was prepared in 2% aqueous acetic acid. A solution of 0.1 M ceric ammonium nitrate in 10 ml of 1 N nitric acid was added followed by a known amount of acrylonitrile drop by drop with continuous stirring. After a specified time, the reaction was stopped and the product was precipitated using sodium hydroxide solution with vigorous stirring. The precipitate was washed with distilled water for several times then filtered and dried.

Experimental Process of Removal of Chromium and Copper

Batch studies were performed with different concentrations of chromium and copper salt to investigate the extent of adsorption. The extent of removal of the two metals was investigated separately changing the adsorbent dose, pH of the solution and time of shaking the adsorbent metal solution mixture. The pH of each solution was adjusted to different values with either NaOH or HCl. The stoppered bottles were agitated at 30°C by orbital shaker at fixed speed, 160 rpm for various time intervals. The adsorbates were separated using Whatman filter paper and supernatant liquid was analyzed for residual concentration of the metals by atomic absorption

spectrophotometer. Triplicate runs differing by less than 1% of all the tests were achieved assuring the reproducibility of the obtained data.

RESULTS AND DISCUSSION

Factors Influencing the Adsorption of Cu(II) and Ni(II) ions

Effect of Adsorbent Dose

The study of effect of adsorbent dose on metal adsorption has shown that adsorption had increased for both the metals with increase in amount of chitosan-g- polyacrylonitrile. The effect of the amount of adsorbent on the removal of Cu^{2+} and Cr^{6+} ions is depicted in the Fig. 1. It seen that the removal of metal ions increases with an increase in the amount of adsorbent. The amount of adsorbent dose varied from 0.5 -4.5g. For chromium, minimum percentage removal was 41.4% for the dose of 1gm to maximum value of 74% for the dose of 5gm, where as for copper, minimum percentage removal was 37.25% for the dose of 1gm to maximum value of 64.5% for the dose of 5gm as shown in Fig. 1. Results showed that the adsorbent dose chitosan-g-copolymer was efficient for maximum removal of Cu^{2+} and Cr^{6+} ions at all levels of adsorbent dose. [23]. Among the two metals chromium gets adsorbed at a higher rate than copper.

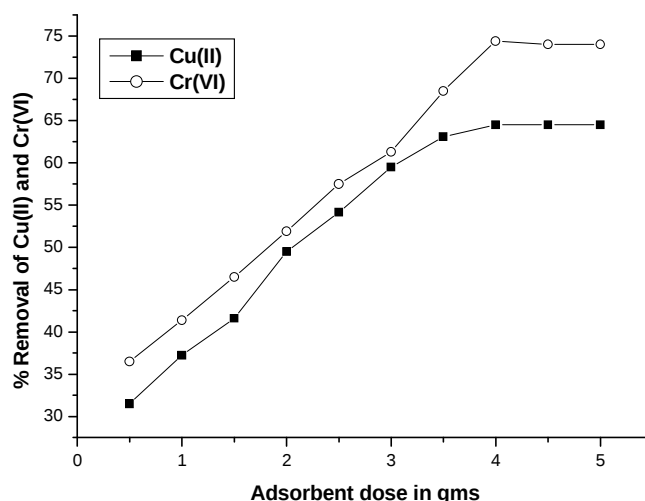


Fig 1: Effect of adsorbent dose on the adsorption of chromium and copper.

Effect of pH

The pH of the solution affects on the surface charge of the adsorbents [23]. It is known that metal species $[\text{M(II)} = \text{Cu(II)}]$ are present in deionised water in the form of M^{2+} , M(OH)_2 [24]. The role of hydrogen ion concentration was examined in solutions at different pH [25]. It was observed that with the increase in the pH of the solution, the extent of metal ions removal increased for the adsorbent. But there was a difference in the trend of the increase. The extent of removal of Cr(VI) and Cu(II) was investigated by varying the pH from 4.0 to 8.5 and the results are shown in the Fig. 2. From Fig. 2, it is observed that pH significantly affects the adsorption process of both metals. The best results were obtained at pH 5.5 for chromium and pH 7 for copper. Increases in metal removal with increase pH can be explained on the basis of a decrease in

competition between proton and metal cations for same functional groups and by 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 hydroxy complexes.

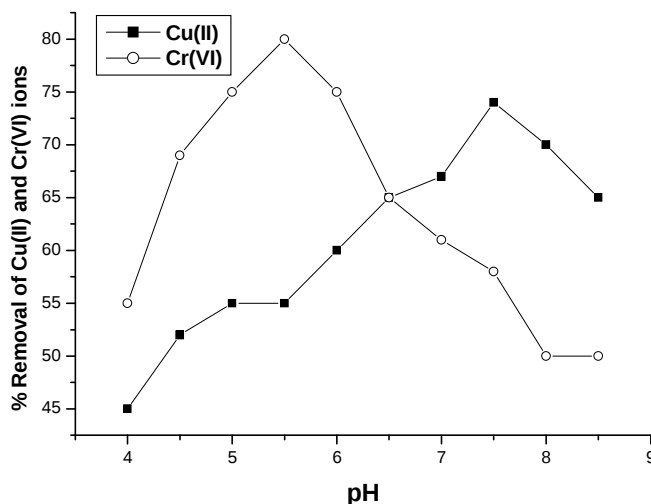


Fig 2: Effect of pH on the adsorption of chromium and copper.

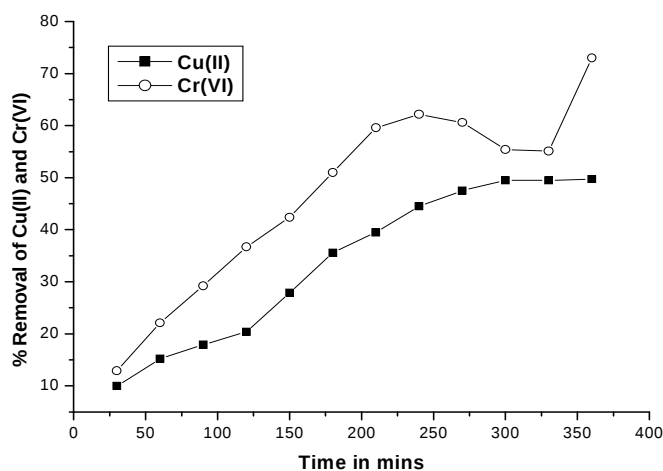


Fig 3: Effect of time on the adsorption of chromium and copper.

Effect of Contact Time

Effect of contact time on adsorption was studied and the results are shown in Fig. 3. Increase in removal efficiency with increase in time of contact can be attributed to the fact that more time becomes available for metal ions to make an attractive complex with chitosan -g- polyacrylonitrile. Fig. 3 depict the effect of contact time on the rate of uptake of Cr(VI) and Cu(II) ions. It was found that the removal of metal ions increased with increase in contact time to some extent. Further increase in contact time did not increase the uptake due to deposition of

metal ions on the available adsorption sites on the adsorbent materials. Preliminary investigations into the uptake of Cr(VI) and Cu(II) ions on the adsorbent materials at their optimum pH values indicate that the process are rapid. Typically 40-70% of the ultimate adsorption capacity occurs within the first hour of contact for both Cr(VI) and Cu(II) ions. This initial rapid adsorption subsequently gives way to a very slow approach to attain equilibrium and saturation is reached in 5-6 hr [25].

Adsorption Kinetics

Kinetic analysis is required to get an insight of the rate of adsorption and the rate limiting step of the transport mechanism, which are primarily used in the modeling, and design of the process. The experimental data was fitted with linearized forms of pseudo-first order (Eq. (1)) (Lagergren equation) [26] and pseudo-second order (Eq. (2)) [27].

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (1)$$

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

where q_e and q_t are the amounts of metal adsorbed (mg g^{-1}) at equilibrium and at time t (min), k_1 (min^{-1}) and k_2 (g mg^{-1}) are the rate constant of pseudo first order and 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 pseudo second order models, respectively. The rate constants k_1 and k_2 can be obtained from the plot of experimental data.

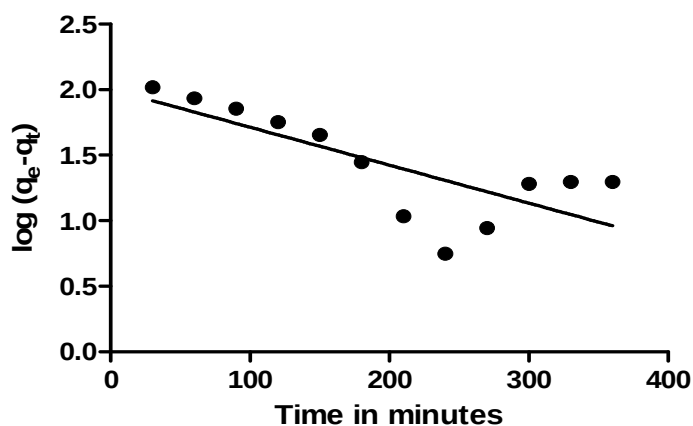


Fig 4: Pseudo-first-order sorption kinetics of Cr (VI) on chitosan-g-polyacrylonitrile.

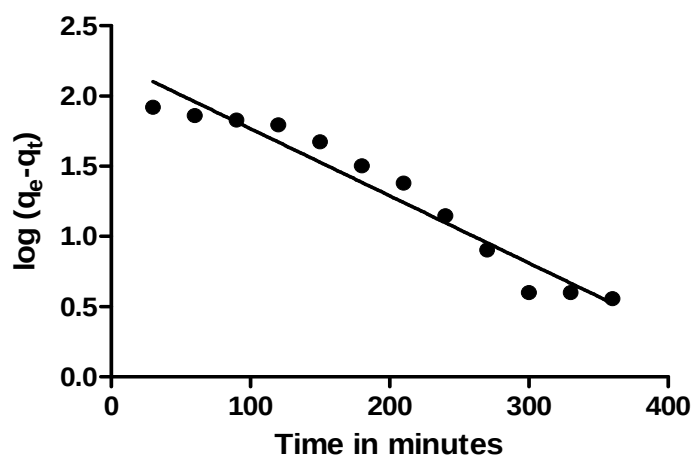


Fig 5: Pseudo-first-order sorption kinetics of Cu(II) on chitosan-g-polyacrylonitrile.

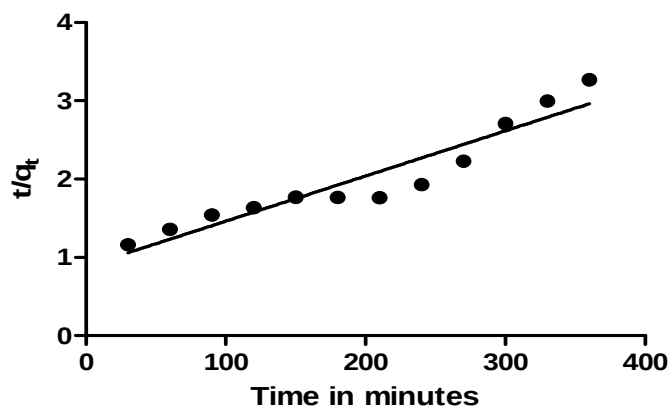


Fig 6: Pseudo-second-order sorption kinetics of Cr(VI) on chitosan-g-polyacrylonitrile.

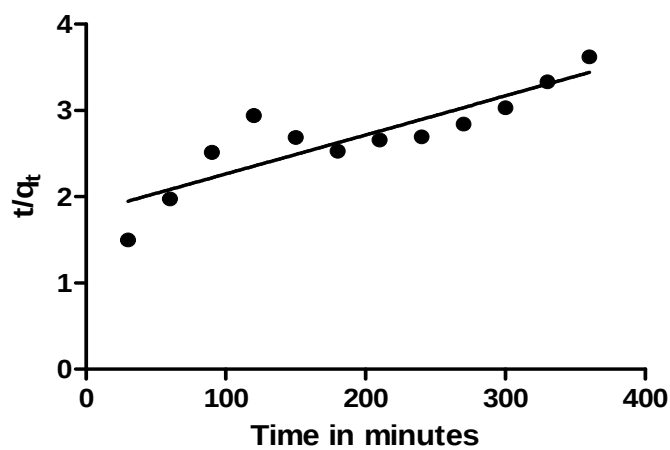


Fig 7: Pseudo-second-order sorption kinetics of Cu(II) on chitosan-g-polyacrylonitrile.

Table 1 Comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models for Cr(VI) and Cu(II) sorption by chitosan-g-polyacrylonitrile

Metal ion	Pseudo-first-order kinetic model			Experimental value	Pseudo-second-order-kinetic model		
	q_e (mg g ⁻¹)	k_1 (min ⁻¹)	R^2	q_e (mg g ⁻¹)	q_e (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R^2
Cr(VI)	691.8	0.0028	0.5835	130	153.4	0.0057	0.8969
Cu(II)	469.4	0.0047	0.9466	103	223.8	0.0063	0.7602

From **Table 1**, it can be seen that the linear correlation coefficients (R^2) of pseudo-first order kinetic model for Cu(II) are high. However, there is large differences between the experimental q_e value and the calculated q_e value, which indicated the pseudo-first order kinetic model was poor fit for Cu(II) adsorption. It can also be found from **Table 1** that R^2 for the pseudo-second order kinetic model for both metals are considerably high, moreover, the calculated q_e values for the pseudo-second order kinetic model are all very closer with the experimental q_e values (Figs. 4-7). These suggested that the adsorption processes of chitosan-g-polyacrylonitrile for Cr(VI) and Cu(II) can be well described by the pseudo-second order kinetic model rather than the pseudo-first-order kinetic model.

Adsorption Isotherm

The application of biosorption process on the commercial scale requires proper quantification of the sorption equilibrium for process simulation. The Langmuir equation has been frequently used to give the sorption equilibrium [28]. 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. To get the equilibrium data, initial metal concentration were varied while the adsorbent mass in each sample was kept constant. The linearised Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constant by the following equation:

$$\frac{C_{eq}}{C_{ads}} = \frac{bC_{eq}}{K_L} + \frac{1}{K_L} \quad (3)$$

$$C_{max} = \frac{K_L}{b} \quad (4)$$

where

C_{ads} = amount of metal ions adsorbed (mg g⁻¹)

C_{eq} = equilibrium concentration of metal ion in solution (mg dm⁻³)

K_L = Langmuir constant (dm³.g⁻¹)

b = Langmuir constant (dm³.g⁻¹)

C_{max} = maximum metal ion to adsorb onto 1g adsorbent (mg.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 [29]. The constants “ b ” and “ K_L ” are the characteristics of the Langmuir equation can be determined from the linearised form of the Langmuir equation (Eq. (3)). A linearised plot of C_{eq}/C_{ads} against C_{eq} gives “ K_L ” and “ b ”

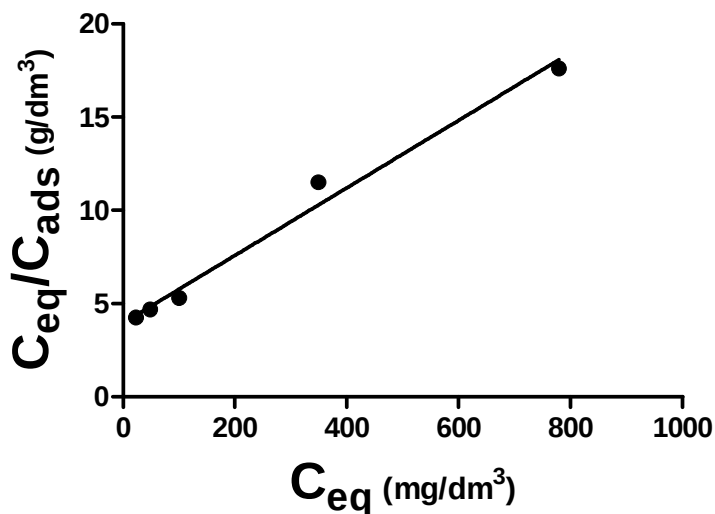


Fig 8: Langmuir isotherm for Chromium

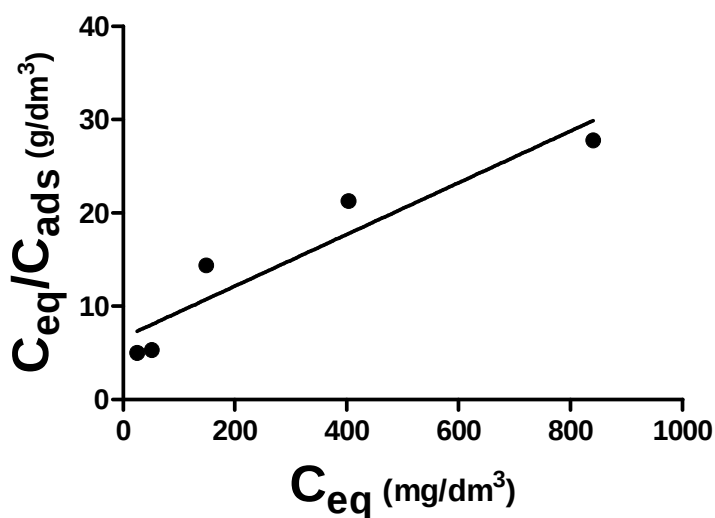


Fig 9: Langmuir isotherm for Copper.

Table 2 Adsorption isotherm constant, $C_{\max}$ and correlation coefficients

Metal ions	Langmuir constants			
	K_L ($\text{dm}^3 \text{g}^{-1}$)	b ($\text{dm}^3 \text{mg}^{-1}$)	$C_{\max}$ (mg g^{-1})	R^2
Cr(VI)	3.963	0.01811	218.82	0.8917
Cu(II)	6.629	0.02770	239.314	0.9854

Langmuir isotherms are shown in Figs. 8 and 9 for chromium and copper, respectively and the parameters are given in Table 2. Linear Langmuir plot indicates the formation of monolayer coverage of adsorbate on the surface of adsorbent. $C_{\max}$ value for copper is high as compared to that of chromium. The values are 239.314 mg of copper per gram of chitosan-g-polyacrylonitrile and 218.82 mg of chromium per gram of chitosan-g-polyacrylonitrile. Value of R^2 shows

correlation or linear relationship. The relationship becomes more linear with the values closer to 1. Thus, it is found that the adsorption of Cr(VI) and Cu(II) onto chitosan-g-polyacrylonitrile correlates well with Langmuir equation.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L that is used to predict if an adsorption system is favourable or unfavourable [30].

The separation factor, R_L is defined by:

$$R_L = \frac{1}{1 + bC_f} \quad (5)$$

where C_f is the final Cr(VI) and Cu(II) concentration (mg dm^{-3}) and b is the Langmuir adsorption equilibrium constant ($\text{dm}^3 \text{mg}^{-1}$). The parameter indicates the isotherm shape according to Table 3.

Table 3. Effect of separation factor on isotherm shape

R_L Values	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

Table 4. 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	0.0662
	500	349	0.1366
	200	100	0.3557
	100	48.5	0.5323
	50	23	0.7059
Cu(II)	1000	848	0.0408
	500	403	0.0822
	200	148.5	0.1955
	100	51.5	0.4121
	50	25	0.5908

The values of R_L calculated for different Cr(VI) and Cu(II) concentration are given in Table 4. If the values are in the range of $0 < R_L < 1$, it indicates that the adsorption of Cr(VI) and Cu(II) onto chitosan-g-polyacrylonitrile is favourable. Thus, chitosan-g-polyacrylonitrile is favourable adsorbent.

CONCLUSION

Graft copolymer of chitosan-g-polyacrylonitrile was successfully synthesized by free radical polymerization using the initiator ceric ammonium nitrate. The graft copolymer was characterized by FTIR and XRD, which elucidated the structure changes in comparison with pure chitosan. The SEM micrograph of grafted chitosan showed fractured and rough surface morphology providing better adsorption sites. TGA and DSC analysis revealed that graft

copolymer had more thermal stability. The results of grafting yield and grafting efficiency from the graph confirm that graft copolymerization has been successively achieved. The present study showed that the chitosan-g-polyacrylonitrile is an effective adsorbent for the removal of Cr(VI) and Cu(II) metal ions from aqueous solutions. The adsorption of Cr(VI) and Cu(II) ions are dependent on initial concentration of the metal ion, adsorbent dose, pH and the contact time. The kinetics and isotherm studies indicated that the pseudo-first-order, pseudo-second-order and the Langmuir model well described the adsorption equilibrium of Cr(VI) and Cu(II) ions on chitosan-g-polyacrylonitrile. Chitosan-g-polyacrylonitrile was found to be a favourable adsorbent.

REFERENCES

- [1] S. Kumar, Water Supply Engineering, Khanna Publishers, New Delhi, **1984**.
- [2] V. Ponnusami, N. Lavanya, M. Meenai, R. Arulgnanaraj, S.N. Srivastava, *Poll. Res.*, **2008**, 27(1), 45.
- [3] M. Vasanthi, M. Sangeetha, R. Kalaiselvi, *J. Ind. Poll. Control*, **2004**, 20(1), 37.
- [4] K. Somasekhara Rao, B. Sreedhar, K. Rajesh, Muppa Ravi, K.N.K. Vani, *Ind. J. Env. Protection*, **2008**, 28(6), 505.
- [5] C.P. Kaushik, Kaushik Namrata, J.K. Sharma, *Nat. Env. Polln. Tech.*, **2005**, 4(2), 163-166.
- [6] L. Dambies, C. Guimon, S. Yiacoumi, E. Guibal, *A Physiochem. Eng. Aspects*, **2001**, 177, 203-214.
- [7] P.K. Dutta, J. Dutta, M.C. Chattopadhyaya, V.S. Tripathi, *J. Polym. Mater.*, **2004**, 21, 321-334.
- [8] N.K. Mathur, C.K. Narang, *J. Chem. Edu.*, **1990**, 67, 938.
- [9] M.A. Meyer, *Prog. Mater. Sci.*, **2007**, 53, 1.
- [10] P.N. Sudha, Chitin, chitosan and derivatives for waste water treatment. In: S.-K. Kim (Ed.), Chitin, Chitosan, Oligosaccharides and their Derivatives (CRC Press, London, **2010**) 561-585.
- [11] H. Caner, H. Hasipoglu, O. Yilmaaz, E. Yilmaaz, *Eur. Polym. J.*, **1998**, 34(3-4), 493-497.
- [12] M.Y. Pedram, J. Retuert, *J. Appl. Polym. Sci.*, **1996**, 63(10), 1321-1326.
- [13] K.I. Shantha, U.K. Bala, K.P. Rao, *Eur. Polym. J.*, **1995**, 31(4), 377.
- [14] T. Sun, W. Xie, P. Xu, *Carbohydr. Polym.*, **2004**, 58(4), 379-382.
- [15] A. Srivastava, J. Tripathy, M. Mishra, K. Behari, *J. Appl. Polym. Sci.*, **2007**, 106(2), 1353-1358.
- [16] J. Tripathy, D.K. Mishra, M.M. Mishra, K. Behari, *Carbohydr. Polym.*, **2008**, 72, 462.
- [17] T.M. Don, C.F. King, W.Y. Chiu, *J. Appl. Polym. Sci.*, **2004**, 86(12), 3057-3063.
- [18] Y.H. Kim, S.H. Kim, C.R. Park, *Bioconjugate Chem.*, **2000**, 12(6), 932-938.
- [19] M.Y. Pedram, J. Retuert, R. Quijada, *Macromol. Chem. Phys.*, **2000**, 201(4), 923-930.
- [20] H.S. Blair, T.K. Guthrie Law, P. Turkington, *J. Appl. Polym. Sci.*, **1981**, 33(2), 641-656.
- [21] A. Mochalova, L. Smirnova, S. Zaitsev, Y. Semchikov, I. Zaitseva, G. Pavlov, *Polym. Sci. Ser. B*, **2007**, 49(9), 232-235.
- [22] Y.Q. Xia, T.Y. Guo, M.D. Song, B.H. Zhang, B.L. Zhang, *Biomacromolecules*, **2005**, 6(5), 2601-2606.
- [23] H. A. Elliott, C. P. Huang, *Water Res.*, **1981**, 15, 849-854.
- [24] V. L. Snoeyink, D. Jenkins, *Water Chemistry*, John Wiley and Sons, New York, **1980**.
- [25] M.N. Rao, A.V. Parwate, A.G. Bhole, *Poll. Res.*, **2001**, 20(4), 669-675.
- [26] S. Lagergren, *Handlingar*, **1898**, 24, 1-39.

- [27] Y.S. Ho, G. McKay, *Process Biochem.* **1999**, 34, 451–465.
- [28] B. Koumanova, P. Peeva, S.I. Allen, K. Gallagher M.J. Healy, *Chem. Technol. Biotechnol.*, **2002**, 77, 539.
- [29] R. Schmuhl, H.M. Krieg, K. Keizer, *WaterSA*, **2001**, 27(1), 1-83.
- [30] W.S.W. Ngah, A. Musa, *J. Appl. Polym. Sci.*, **1998**, 69, 2305-2310.