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Separation of chromium and copper from wastewater using poly acrylonitrile blended chitosan

S. Raghunadh Acharyulu[a], N. Prakash*[b], P. N. Sudha[c] and N. G. Renganathan[b]

[a]Department of Chemistry, Sri Chandrasekharendra Saraswathi Viswa Mahavidyalaya (SCSVMV) University, Kanchipuram, Tamil Nadu, India
[b]Department of Chemistry, Vel Tech University, Chennai, India
[c]Department of Chemistry, D.K.M. College for Women, Vellore, India

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ABSTRACT

Heavy metal contamination is a potential threat to drinking water sources. Chromium (VI) is more water soluble, it easily enters living cells and is much more toxic than Chromium (III). In the same way, the presence of excess copper metal ions in the human body leads to lot of toxicological effects such as hepatocirrhosis. In the present study, the blending of cross linked Chitosan with copolymers Poly AcryloNitrile (PAN) has been synthesized in presence of cross linking agent glutaraldehyde in 2% aqueous acetic acid solution. The synthesized copolymer blend was subjected to the analytical techniques like Fourier Transform Infrared Spectroscopy (FT-IR), and XRD studies to confirm the formation of copolymer blends. The prepared copolymer blend was subjected to heavy metal contaminated wastewater and the results revealed that the prepared copolymer blends are excellent in removing all the metal ions by adsorption. Hence the cross linked Chitosan-Poly acrylonitrile (CS/PAN) copolymer blends could successfully open a way for the Chromium (VI) and Copper (II) ions removal from the aqueous solutions. The adsorption capacity of the copolymer blends were determined by using Langmuir and Freundlich adsorption isotherms.

Keywords: Chitosan (CS), Poly acrylonitrile (PAN), heavy metals removal, Kinetic analysis

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INTRODUCTION

Spurious and intensified industrial activity in the recent years is greatly contributing to an increase in the discharge of toxic compounds in the natural environment, particularly in aquatic systems. Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain.

Heavy metals are dangerous because they tend to bioaccumulation. Heavy metals such as Hg, Cr, Pb, Ni, Cu, Cd and Zn are usually associated with toxicity [1, 2]. Chromium (Cr) exists in oxidation states (di-, tri-, penta-, and hexa) trivalent chromium together with the hexavalent state can be mainly present in the aquatic environment. Trivalent chromium acts as the micro nutrients which is essential for glycolysis whereas hexavalent chromium is 500 times toxic than trivalent chromium. It is carcinogenic and mutagenic as well as being a strong oxidizing agent which irritates plant and animal tissues even in small quantities. It diffuses rapidly through soil and aquatic environments as well as readily passing through skin. In human body, copper is maintained in homeostasis [3]. If the percentage of the Copper ions in the body increases then it would cause toxic effects such as haemolysis, jaundice and even death [4]. Most recently, the study indicates that the overload of common copper in vivo can induce a set of toxicological activities such as hepatocirrhosis [5], changes in lipid profile, oxidative stress, renal dysfunction [6] and stimulation of mucous membrane of alimentary canal.

Effective removal of these heavy metals from the wastewaters has therefore received much attention in recent times. [7, 8], different technologies have evolved for the removal of heavy metals from water, such as ion–exchange, precipitation, flotation, solvent extraction, adsorption and electrolytic methods [9, 10]. More attention has recently been focused on biopolymers and bio adsorbents. These are naturally produced and have no adverse impact on human or environmental health. Polysaccharides like chitosan, a natural amino polymer plays an important role in treatment of waste water [11-15].

Chitin poly (1->4)-2-acetamide-2-deoxy-β-D-glucan is a natural polymer extracted commercially from the shells of crustaceans such as prawns, crabs, krill, insects and shrimps [16]. Chitosan poly (1->4)-2-amino-2-deoxy-β-D-glucan is prepared from chitin by partially deacetylating its acetamido groups with strong alkaline solution. Chitin and chitosan are widely used for the treatment of wastewater which decreases the chemical oxygen demand, total nitrogen and destroy the microbial population [15]. Chitosan has its limitations like acidic solubility, low thermal and mechanical stability. To rectify these drawbacks, chitosan can be modified physically and chemically. Nowadays lot of attention has been paid on chemical modification of chitosan. One such important modification is polymer blending. Blending of cross linked chitosan with copolymers like polyacrylonitrile and polystyrene is quite promising. In chitosan both hydroxyl and amino groups are possible sites for the reaction to incorporate new and desired functional groups [18-19]. Blending of synthetic polymers on to chitosan can introduce desired properties and enlarge the field of applications by choosing various types of side chains. In the present work chitosan which was cross linked with glutaraldehyde has been blended with the copolymers polyacrylonitrile and polystyrene with an aim to develop a product, which could be used for the removal of Cu(II) and Cr(VI) ions from wastewater. The polymer blend obtained was subjected to various analytical techniques such as FTIR and XRD to confirm the blend formation. The equilibrium adsorption of Cr(II) and Cr(VI) ions onto chitosan-coplymer blends from wastewater was investigated. The adsorption capacity for the adsorption of Cu(II) and Cr (VI) ions onto chitosan blends were determined using Langmuir and Freundlich equations.

MATERIALS AND METHODS

Materials: Chitosan was a kind gift from Indian Sea food, Cochin, Kerala, India. The cross linking agent glutaraldehyde was obtained from Central Drug House Private Ltd, Mumbai. Polyacrylonitrile and polystyrene were purchased from Sigma Aldrich, Bangalore, India. All the chemicals used in the study are of analytical grade.

Preparation of cross linked chitosan: Initially chitosan solution was prepared by dissolving 2g of Chitosan in 50 ml of 2% aq. acetic acid solution with constant stirring for 4 h to form a homogeneous solution. Then 15 ml of cross linking agent glutaraldehyde was added to the above prepared Chitosan solution (100 ml) which was then stirred for 20 min using a magnetic stirrer.

Preparation of copolymer blends: The above prepared chitosan solution (100 ml), 2 g PAN (Aldrich 18131-5) and 50 ml of dimethylformamide (DMF) were stirred for 4 h in a magnetic stirrer to form a homogenous solution. The resultant mixture was kept for 4 h and the solution was casted in polyacrylonitrile plates and dried in vacuum at 70°C. Similar procedure was adopted for the blend of polystyrene in different weight ratios (1:1) & (1:2).

Characterization of Polymer blends: The prepared copolymer blends were characterized using two excellent analytical techniques such as FT-IR and XRD. The instrument used for to determine the FT-IR spectroscopy of copolymer blends in the present study is Perkiln- Elmer spectrophotometer. The FT-IR spectra was obtained in solid state using KBr pellets in the wave length between 400 cm^{-1} to 4000 cm^{-1} . The physical nature of the copolymer blends were investigated using XRD studies.

Physical characteristics of copolymer blends: The prepared copolymer blends were appeared as off-white solids, which have more acidic solubility than chitosan alone. The adsorption capacity of these copolymer blends also would increase because of the good surface area due to the blending of copolymers.

RESULTS AND DISCUSSION

FTIR Characterization: The cross linked chitosan blended with polyacrylonitrile in two different ratios (1:1) & (1:2) are shown in the Fig. 1 & 2. When the copolymer is blended with chitosan it forms a strong hydrogen bond with the free amine groups present in chitosan, as shown by the shift to 2342.25 cm^{-1} from 2387.19 cm^{-1}.The C=O bond becomes stronger and it is shifted to higher frequencies(1624 cm^{-1}). This is due to the propagation of electrons from the acrylo nitrile group into nitrogen present in free amine. The frequency which is observed at 2140.98 cm^{-1} is due to nitrile group in PAN. This moderation is due to inter molecular hydrogen bond with the acidic proton present in free amine group in chitosan. When the percentage ratio of PAN increases then the NH_3^+ stretching frequency becomes very weak and almost disappears in the spectra and also the C=O stretching frequency is shifted to much higher frequencies (1627 cm^{-1}). These observations clearly indicate complete blending of chitosan with PAN.

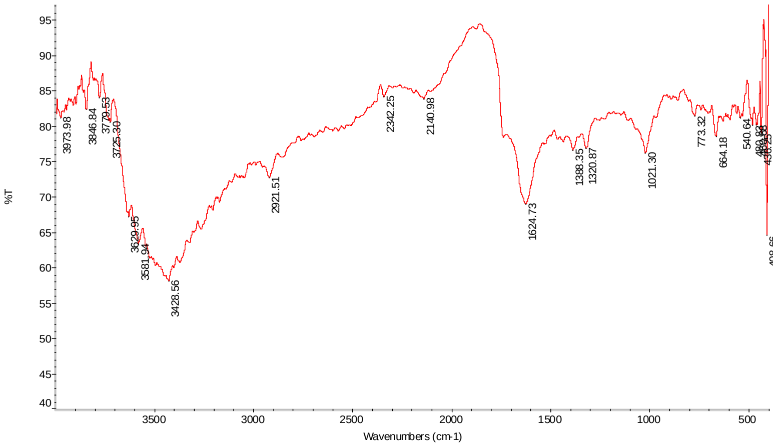

Fig. 1 1:1 ratio FTIR spectra of cross linked chitosan with polyacrylonitrile

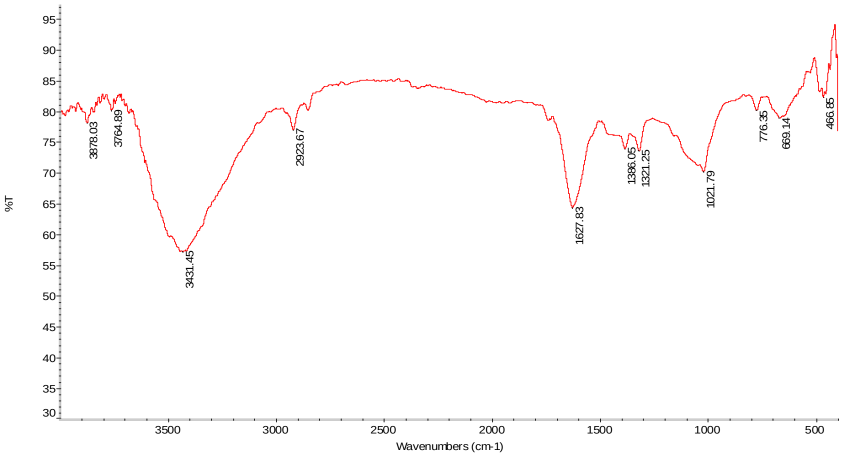

Fig. 2 1:2 ratio FTIR spectra of cross linked chitosan with polyacrylonitrile

XRD analysis of copolymer blends: Fig. 3 shows XRD spectra of pure chitosan and Fig. 4 shows the XRD spectra of 1:1 ratio of cross linked chitosan-polyacrylonitrile blend in the presence of cross-linking agent glutaraldehyde. This shows a peak at $2\theta=26$. This is short and broad. This indicates that the nature of the polymer blend is in amorphous phase. Fig. 5 shows the XRD spectra of 1:2 ratio of cross linked chitosan polyacrylonitrile blend in the presence of cross-linking agent glutaraldehyde. A short and broad peak appears at $2\theta=25$. The lower 2θ value indicates the poor crystallinity of the copolymer blend, which is very good for heavy metal adsorption. The more amorphous nature of the copolymer blend the better is the adsorption of the heavy metal ions.

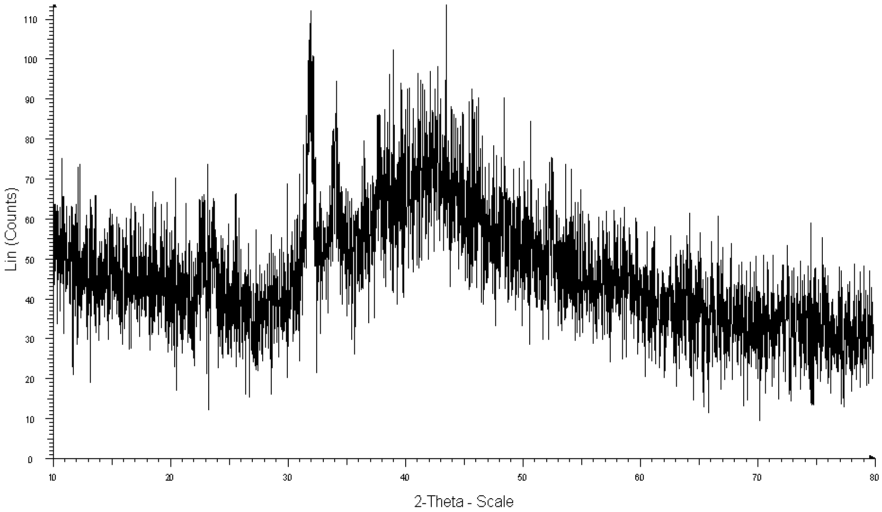

Fig. 3 XRD spectra of cross linked chitosan with glutaraldehyde

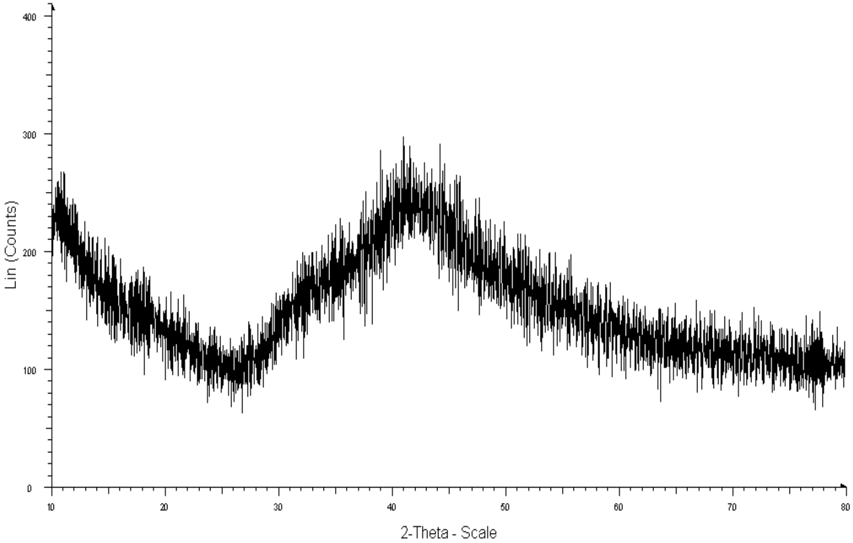

Fig. 4 XRD spectra of 1:1 ratio of cross linked chitosan-polyacrylonitrile blend

Thermo gravimetric analysis (TGA): Fig. 6 shows TGA spectra of pure chitosan, Fig. 7 and 8 show the TGA spectra of 1:1 & 1:2 ratio of cross linked chitosan-polyacrylonitrile blend in the presence of cross-linking agent glutaraldehyde. TGA has been used to ascertain the thermal stability of the polymer. So the prepared films were subjected to TGA analysis [20]. Four stages of degradation are observed. Initially a moisture loss followed by ternary moiety disintegrating to a binary and then to various decomposed products was followed. The first stage appeared around 100^0C, corresponding to the evaporation of water adsorbed and/or weakly hydrogen-bonded water. The second weight loss at about 230^0C was probably due to the ternary moiety disintegrating to a binary moiety. Then the significant mass loss at about 425^0C was probably due to the depolymerization of the prepared blend followed by decomposition of the pyranose rings. The last step was seen at around 575^0C. The blend prepared in the presence of crosslinking agent showed high thermal stability. Results revealed the increase in the thermal stability of the polymer blend in the presence of cross-linking agent.

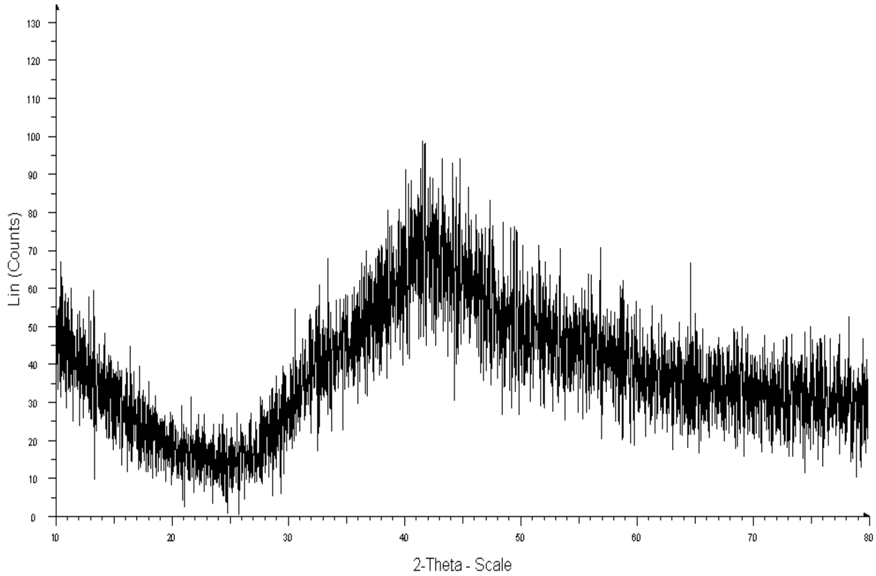

Fig. 5 XRD spectra of 1:2 ratio of cross linked chitosan-polyacrylonitrile blend

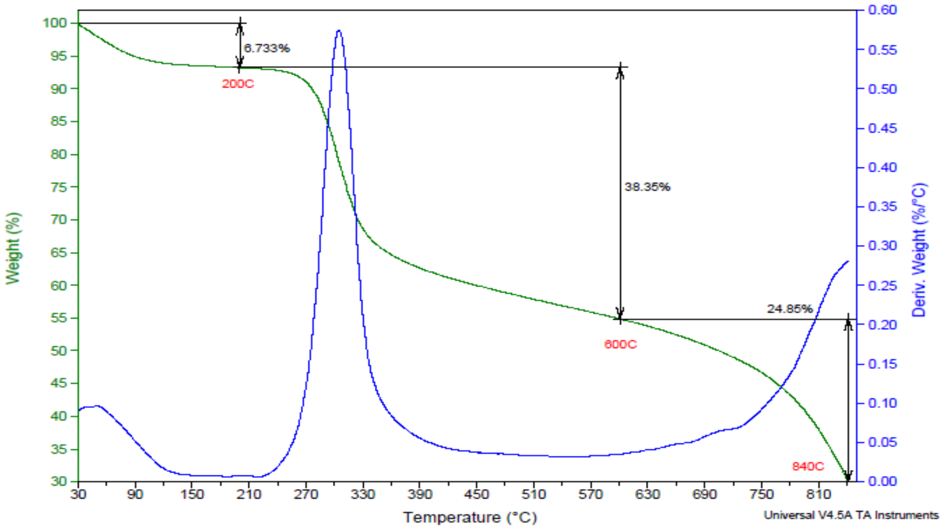

Fig. 6 TG/DTG of pure chitosan blend

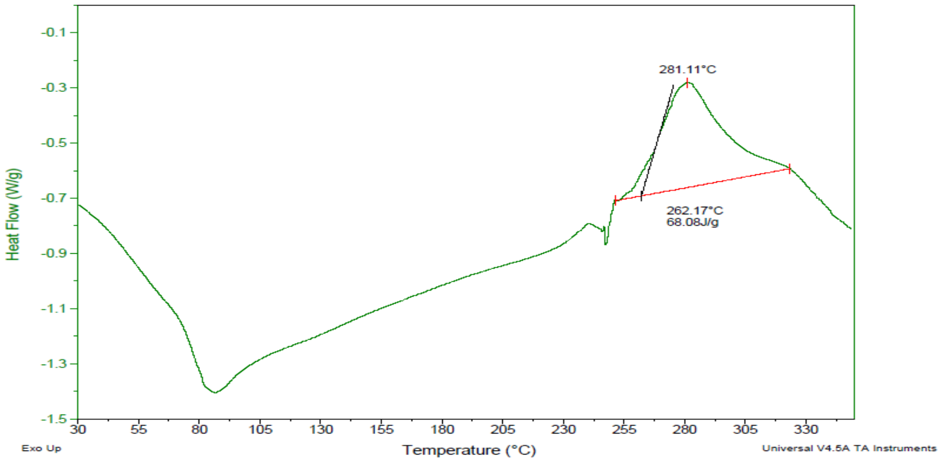

Fig. 7 TG/DTG of chitosan, Polyacrylonitrile blend ration (1:1)

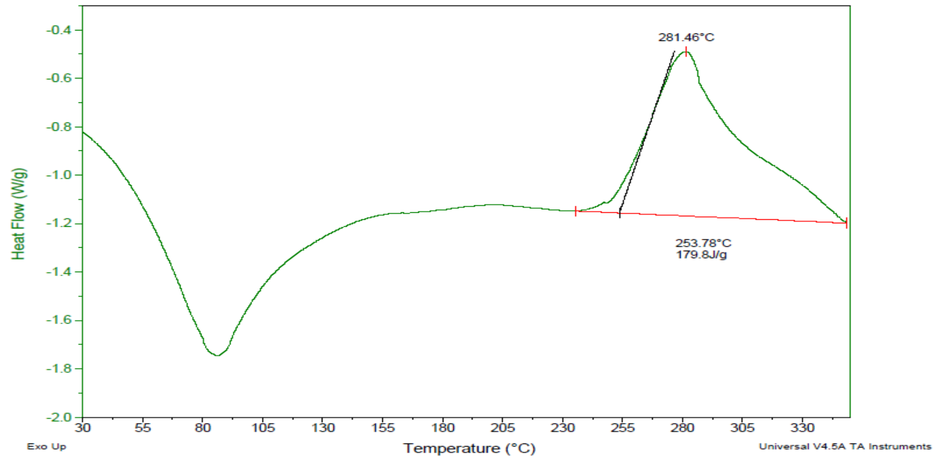

Fig. 8 TG/DTG of chitosan, Polyacrylonitrile blend ration (1:2)

Differential Scanning Calorimetry (DSC): DSC studies help to understand the thermal behavior of the polymer blend as shown in Fig. 9 & 11 There are two separate regions, one at 35-75 ^{0}C and the other at 80−160°C. The peak at 60^{0}C may be due to melting point of PAN. There are two other peaks around 100^{0}C. These may be due to chitosan and blend film. Depending on PAN content the peaks due to pure chitosan shifts to a lower region and the other one shift to higher region. It is also reported [21, 22] that the two peaks may be due to evaporation of solvent. The peak at 270^{0}C is an exothermic peak and this is due to degradation of the main chain and this is for pure chitosan. With the addition of PAN this exothermic peak is shifted to higher temperature, to 275^{0}C. If excess PAN is present this peak would have shifted to low temperature. The endothermic peak and the glass transition temperature of the samples are expected to be shifted to the higher region. This suggests that the thermal stability of the blend is higher.

The pure CS blend films showed a relatively large and sharp endothermic curve with a peak at 89^{0}C.

Endothermic curve - broad and obtuse is shifted towards the low temperature thus indicating that the crystalline nature of CS was decreased by the addition of PAN. It was observed that the peaks of the endothermic curves shifted towards the low temperature from 89^{0}C to 75^{0}C with increasing PEG content in the blend. This demonstrated that the PAN content in the blend lead to decreasing tendency of crystallization of the blend. Also it was observed that the peaks of the endothermic curves are shifted towards the high temperature 92^{0}C with increasing CS content in the blend. Single T_g in this curve shows a good polymer – polymer miscibility, The Tg increases due to effective crosslinking.

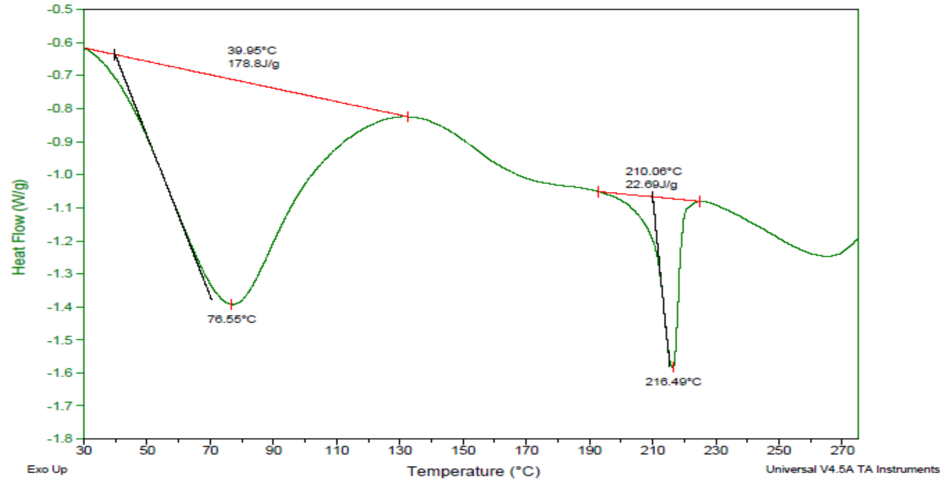

Fig. 9 DSC of pure chitosan blend

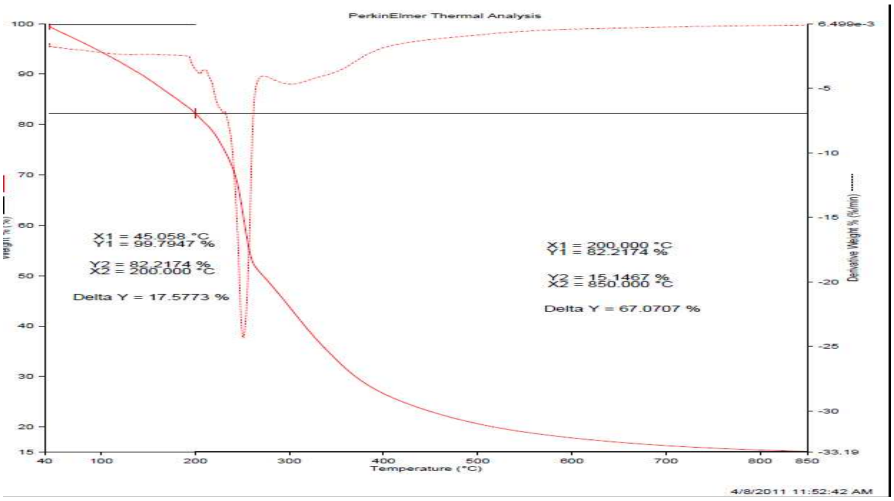

Fig. 10 DSC of chitosan, Polyacrylonitrile blend ration (1:1)

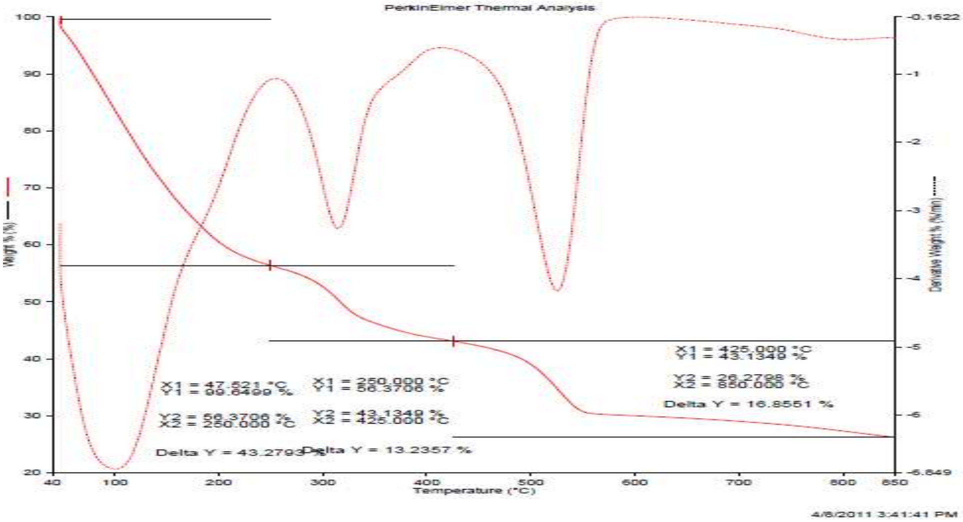

Fig. 11 DSC of chitosan, Polyacrylonitrile blend ration (1:2)

Effect of contact time on the adsorption of chromium and copper ions using CS/PAN copolymer blend

The percentage removal of the metal ions in the electroplating industry effluent with respect to contact is shown in Fig. 12. The Adsorption efficiency of Chromium (VI) and Copper (II) with the contact time using CCS/PAN copolymer blend is Fig. 12. The efficiency increases with the increase of contact time.

An active metal complex with metal ions is formed since more time is made available as contact time. Initial removal of the metal from the solutions is very fast. However, as the contact time increases the efficiency of removal decreases. This is due to the decrease of active sites on the blend for the adsorption of metal ions. This is the equilibrium point, one of the important parameter which is a useful in the economical removal of heavy metals from waste water.

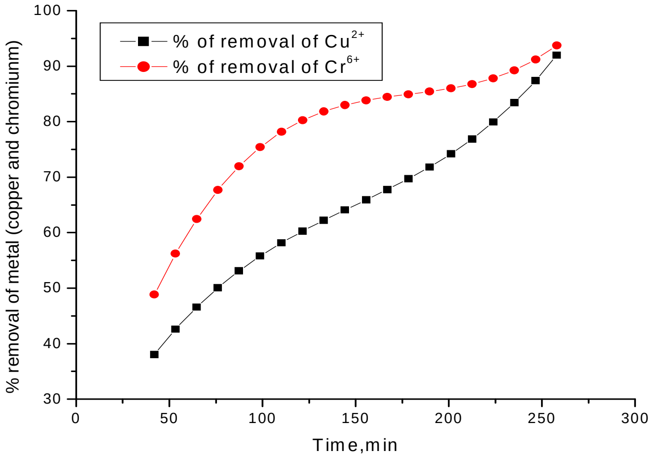

Fig. 12 Effect of time in the adsorption of Cr^{+6} and Cu^{+2} ions using CS/PAN copolymer blend

Effect of adsorbent dosage on the adsorption of Cr (VI) AND Cu(II) ions using CS/PAN blend

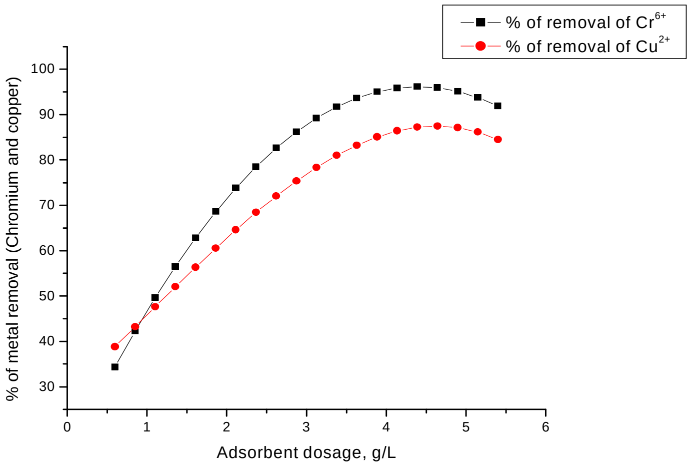

Fig. 13 Effect of Adsorbent dosage in the adsorption of Cr^{+6} and Cu^{+2} ions using CS/PAN copolymer blend

The effect of adsorbent dosage on the wastewater treatment is shown in the Fig. 13. As the adsorbent dosage increases the surface area and the number of possible sites for the metal ion adsorption also increases. When the adsorbent dosage increases from 1g/L to 5g/L then almost 95% of the metal ions are removed.

Effect of pH on the adsorption of Cr (VI) and Cu (II) ions using CS/PAN blend

Fig. 14 shows the effect of pH in the adsorption of chromium and copper from wastewater using CS/PAN polymer blend. The hydrogen and hydroxyl ions are adsorbed quite strongly, and therefore the adsorptions of other ions are affected by the pH of the solution [23]. It is observed that with the increase in the pH of the solution, the extent of metal ions removal increases. As shown in the percentage removal of the metal ions from the industrial effluent is increased with the increase of pH upto 5 and afterwards the efficiency of adsorption decreases. This is explained from the fact that there is a competition between the protons from the acidic solution and the metal cations for the same functional groups on the surface and also due to the lower repulsion on the surface the adsorption efficiency of the metal ions increases with the increase of pH. The adsorption of metal ions will decrease by the adsorbent with further increase of pH because of the soluble hydroxyl complexes.

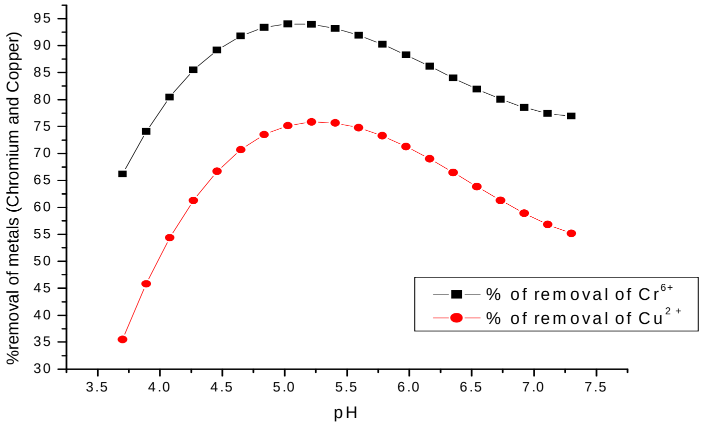

Fig. 14 Effect of pH in the adsorption of Cr^{+6} and Cu^{+2} ions using CS/PAN copolymer blend

Langmuir Adsorption Isotherm

The adsorption involves the attachment of only one layer of molecules to the surface, i.e. monolayer adsorption. Adsorption is reversible and the adsorbed molecule cannot migrate across the surface or interact with neighboring molecules [24, 25].

According to the above assumptions he derived an equation

$$C_{ads} = \frac{K_L C_{eq}}{1+bC_{eq}} \qquad 3$$

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

$$\frac{C_{eq}}{C_{ads}} = \frac{bC_{eq}}{K_L} + 1/K_L \qquad 4$$

$$C_{max} = K_L/b \qquad 5$$

Where, C_{ads} = amount of metal ions adsorbed (mg·g^{-1}), C_{eq} = equilibrium concentration of metal ions in solution (mg·dm^{-3}), K_L = Langmuir constant (dm^3·g^{-1}), b = Langmuir constant (dm^3·mg), C_{max} = maximum metal ions to adsorb onto 1 g chitosan (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 [26]. At the optimum conditions of adsorbent dose and the Ph the copper and chromium solutions with different concentrations were agitated and the solution from the bottle was taken to analyse the unabsorbed chromium and copper at equilibrium. A plot of C_{eq}/C_{ads} vs C_{eq} confirming the applicability of the Langmuir adsorption isotherm. The equilibrium parameter R_L is used to determine whether the adsorption isotherm is favourable or unfavourable [27] it was calculated using the following formula.

$$R_L = 1 + bC_f \qquad 6$$

Where C_f is the final Cr(VI) and Cu(II) concentration (mg/dm^3) and b is the Langmuir adsorption equilibrium constant (dm^3/mg). In the present study the R_L values obtained in the adsorption of Cr(VI) and Cu(II) ions by using both the blends CS/PAN are less than one(R_L<1), So the Langmuir adsorption is suitable for both blends. Fig. 15 and 16 showLangmuir adsorption of chromium and copper and the Table 1-3 indicate various parameters of chromium and copper.

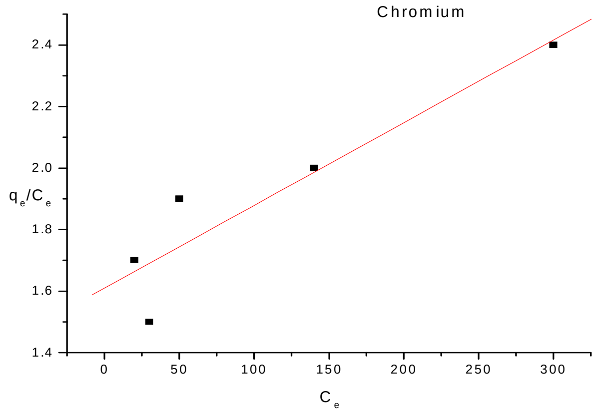

Fig. 15 Langmuir plot for the adsorption of Cr(VI) ions onto CS/PAN copolymer blend

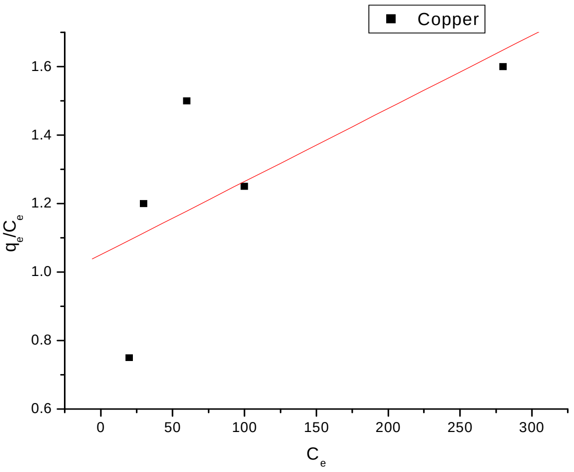

Fig. 16 Langmuir plot for the adsorption of Cu (II) ions onto CS/PAN copolymer blend

Table 1 Adsorption isotherm constant, C_{max} and correlation coefficients for removal of Cr (VI) and Cu (II) using CS/PAN copolymer blend

Metal ion	Langmuir constants			
	K_L (dm^3/g)	b (dm^3/mg)	C_{max} (mg/g)	R^2
Cr(VI)	0.61690	0.0014935	413.05	0.8630
Cu(II)	0.9688	0.002953	328.07	0.6968

Table 2 R_L Values based on Langmuir adsorption isotherm for the removal of Cr (VI) ions using CS/PAN Copolymer blend

Metal ion	Initial concentration(Co)	Final Concentration(C_f)	R_L Values
Cr (VI) metal ions	1000	320	0.67662
	500	145	0.82199
	200	55	0.92409
	100	23	0.96679
	50	12.5	0.98167

Table 3 R_L Values based on Langmuir adsorption isotherm for the removal of Cu (II) ions using CS/PAN Copolymer blend

Metal ion	Initial concentration(C_o)	Final Concentration(C_f)	R_L Values
Cu (II) metal ions	1000	265	0.5610
	500	105	0.7633
	200	45	0.8827
	100	19	0.9468
	50	6.5	0.9812

Freundlich adsorption isotherm

Freundlich adsorption isotherm is obeyed by the adsorptions where the adsorbate forms a monomolecular layer on the surface of the adsorbent. According to this model the adsorbed mass per mass of adsorbent can express by a power law function of the solute concentration as.

$$q_e = K_F \, C_e^{1/n} \qquad 7$$

Where, K_F = Freundlich constant related with adsorption capacity (mg/g), n = heterogeneity, coefficient (dimensionless) for linearization of the data.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad 8$$

The plot of log *qe* (C_e/Y_e) versus log *Ce* has a slope with the value of 1/*n* and an Intercept magnitude of log K_F

q_e = amount of metal ion adsorbed ($mg \cdot g^{-1}$), C_e = equilibrium concentration in solution ($mg \cdot dm^{-3}$), 1/n = Freundlich constant ($mg \cdot g^{-1}$), K_F = Freundlich constant ($g \cdot dm^{-3}$).

According to this adsorption model
(i) At low pressure, the extent of adsorption varies linearly with pressure. $q_e \propto p'$
(ii) At high pressure, it becomes independent of pressure. $q_e \propto p_o$
(iii) At moderate pressure q_e depends upon pressure raised to powers qe $\propto p^{1/n}$

According to this adsorption method ‘n’ is always greater than one, indicating that the amount of the adsorbate adsorbed does not increase as rapidly as the pressure and this value of *n*, falling in the range of 1–10 indicates favourable biosorption [29]. The numerical value of 1/n < 1 indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. In this present study the experimental data were well fitted in the Freundlich adsorption model and the values of ‘n’ (As shown in the tables 4) for both the copolymer blends CS/PAN and CS/PST are greater than one (n>1) indicates that it is a favorable biosorption. Fig. 17 and 18 are well fitted in the Freundlich adsorption model.

Table 4 Frendlich constants for CS/PAN copolymer copolymer blend

Metal ions	Frendlich constants		
	K_F	n	R^2
Cr(VI)	1.331	1.140	0.9965
Cu (II)	1.760	1.266	0.9884

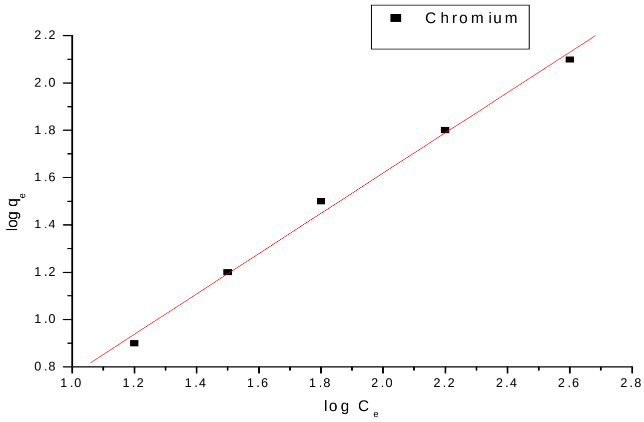

Fig. 17 Frendlich plot for the adsorption of Cr(VI) ions onto CS/PAN copolymer blend

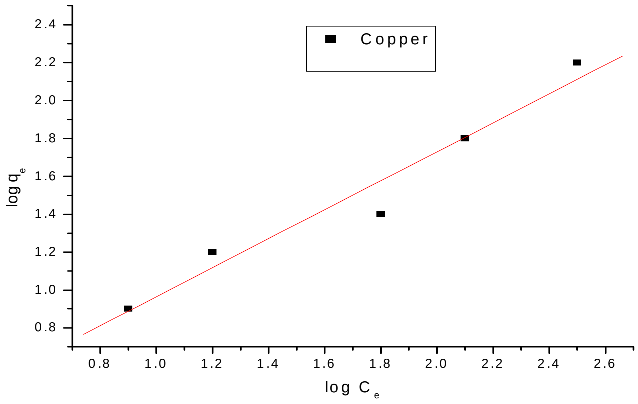

Fig. 18 Freundlich plot for the adsorption of Cu (II) ions onto CS/PAN copolymer blend

CONCLUSION

The present study has proven the formation of crosslinked chitosan-polyacrylo nitrile blend through FT-IR and XRD studies. The effect of physical properties like pH, contact time and adsorbent dosage on the adsorption of Cr (VI) and Cu (II) metal ions have been successfully studied. The adsorption capacities of these polymer blends in the uptake of metal ions were plotted on Langmuir and Freundlich adsorption isotherms. The chromium metal ions were adsorbed more when compared with the copper metal ions by copolymer blend according to Langmuir adsorption isotherm. The adsorption values were well fitted in Freundlich adsorption isotherm when compared with Langmuir adsorption isotherm. So according to this study this copolymer adsorption was a multilayer adsorption. The study also proves the effective heavy metal ion removal.

REFERENCES

[1] I. Borneff , Engel hordt, K.Griemw (**1968**), *Arch.Hyg.*152.45-53.
[2] California Department of health services (**1987**), Drinking water quality monitoring data 1984-1996, Annual status report.
[3] B. Jesse, R.L. Mary, **2004**. *J. Nutr. Biochem*, 15, 316–322.
[4] Zhen Chena, Huan Menga, Gengmei Xing a, Chunying Chena, Yuliang Zhaoa,e, Guang Jia b, Tiancheng Wang d, Hui Yuan a, Chang Ye a, Feng Zhaoa, Zhifang Chai a, Chuanfeng Zhuc, Xiaohong Fang c, Baocheng Mac, Lijun Wan(**2006**), *Toxicology Letters*, 163, 109–120.
[5] P.Z. Bjorn, H.D. Hermann, L. Max, S.Heide, K.G. Barabara, D. Hartmut, (**2003**). *Sci. Total Environ.* 302, 127–144.

[6] Sachin R. Kumbhoje, Swapneel B. Sonone, Suhas S. Awati, Rajanikant B. Ghotane and Shitalkumar S. Patil (**2013**). *Der Pharma Chemica*, 5(3), 256-260.
[7] J.S. Yang, T.S. Kwon, J.W. Yang (**2007**). *Desalination* 206, 245–250.
[8] U.C. Ghosh (**2005**). 31, 597–602.
[9] N.N. Mamdouth, T.E. Kamar, E.E. Ebrahiem (**2004**). *Adsorpt. Sci. Technol*, 22, 25–37.
[10] M. Kobya (**2004**). *Adsorpt. Sci. Technol*, 22, 54–63.
[11] H. Meye, W. Batte and M. Schlaak.M (**2000**). *Advances in chitin science*, 4, 153-158.
[12] G. Crini and P.M. Badot (**2008**). *Progress in polymer science*, 33, 399-447.
[13] W.O. David, F.O. Thomas and B. Colin.B (**2008**). *Bioresource technology*, 99, 6709-6724.
[14] V.K. Gupta, Arunima Nayak. **2012**. *Chem. Eng. J*, 180: 81–90.
[15] K.H. Chu **2002**. *J. Hazard. Mater B* 90, 77–95.
[16] F. Wu, R. Tseng, R. Juang (**2000**). *J. Hazard. Mater* B, 73, 63 – 75.
[17] E. Guibal (**2004**). *Sep. Purif. Technol* 38, 43–74.
[18] E.P Kunkoro, J. Roussy , E. Guibal (**2005**). *Sep. Sci.Technol.* 40, 659–684.
[19] F. Wu, T. Tsung and R. Juang (**2000**). *J. Hazard. Mater. B* 73:63-75.
[20] A. Shanmugapriya, M. Hemalatha, B. Scholastica and T. Augustine Arul Prasad (**2013**). *Der Pharma Chemica*, 5(3), 141-155.
[21] Nagan Prakash, Srinivasan Latha, Peru N. Sudha and N. Gopalan Renganathan (**2013**). Environ.Sci. Pollu.Res, 20(2), 925-38.
[22] N. Prakash, P.N. Sudha and N. G. Renganathan (**2011**). Environ.Sci. Pollu.Res, 19(7), 2930-41.
[23] H. Yu, G.H. Covey and A.J. O'Connor (**2001**). *Appita Journal*, 54,511–517.
[24] J. Febrianto, A.N. Kosasih, J. Sunarso, Y. Ju, N. Indraswati and S. Ismadji (**2009**). *J. Hazard.Materi* (162), 616-645.
[25] A. Shanmugapriya, M. Hemalatha, B. Scholastica and T. Augustine Arul Prasad (**2013**). *Der Pharma Chemica*, 5(3), 141-155.
[26] R. Schmuchl, H.M. Krieg, H.M. Keizer (**2001**). *Water SA*, 27(1), 1–83.
[27] W. S. Wan Ngah, A. Musa (**1998**). *J. App. Polym. Sci*, 69(12):2305-2310.
[28] M.A. Hanif, R. Nadeema, M.N. Zafar, K. Akhtar, H.N. Bhatti. **2007**. *J. Hazard. Mater*, 145: 501–505.