Synthesis of Hydroxyethyl Starch-g-Polyacrylamide (HES-g-PAM) and its Application in Removal of Heavy Metal Ions

B. R. De[1]●, H. Kolya [2] and T. Tripathy[2]

[1]Department of Chemistry, Vidyasagar University,
Midnapore, Paschim Medinipur-721102
Email: brdranjan@yahoo.com
[2]Department of Chemistry, Midnapore College, Midnapore,
Paschim Medinipur-721101

ABSTRACT

Hydroxyethyl starch-g-polyacrylamide (HES-g-PAM) was synthesized by ceric ion induced solution polymerization technique. The graft copolymer was characterized by IR-spectroscopy and intrinsic viscosity measurement. The copolymer was used in removal of heavy metal ions from their solutions. The effect of treatment time on the metal ion absorption was studied. The result shows that metal ion removal capacity of the graft copolymer (mmole/g of the graft copolymer) follows the order $Cu^{+2} > Fe^{+2} > Ni^{+2}$.

Key words: Hydroxyethyl starch, Polyacrylamide, Graft Copolymer.

1. Introduction

Heavy metal contamination exists in aqueous waste streams in many industries, such as metal plating facilities, mining operations and tanneries. The soils surrounding many military bases are also contaminated and pose a risk of metals ground water and surface water contamination. Some metals associated with these activities are cadmium (Cd), Chromium (Cr), Lead (Pb), Mercury (Hg). Heavy metals are not biodegradable and tend to accumulate in living organism, carrying various diseases and disorders.

Treatment process for metals contained waste streams includes chemical precipitation, membrane filtration, ion-exchange carbon adsorption, reverse osmosis and solvent extraction[1]. These methods are relatively expensive. Therefore cost effective alternative technologies or sorbents for treatment of metals contained waste streams are needed. So, there is research interest in using alternative low cost

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● Corresponding author

effective methods for water clearing process. Water-soluble synthetic and natural macromolecules are among the most efficient materials used as flocculants in the process of water clarification[2]. The attempts have been made in the past decades to combine by grafting the best properties of synthetic and natural polymers.[3] It was also concluded that by grafting flexible polyacrylamide chains onto the various polysaccharide backbones it is possible to develop efficient and shear stable flocculating agents for water treatment in industrial effluents and mineral processing[4,5,6].

Various water soluble synthetic polymers like polyacrylamide, polyacrylic acid, polystyrene sulphonic acid etc. as well as various polysaccharides[7,8,9] have on their chains ligands capable to coordinating sites in that material are vary high. Metals are adsorbed at the polymeric backbone mainly by secondary bonding interactions like hydrogen bonding, coordinate bonding involving the metal ions and the electron donating groups present at the polymer. In polyacrylamide the $-NH_2$ groups, in polyacrylic acid the $-COO^-$ and $-COOH$ groups and in polystyrene sulphonic acid the $-SO_3H$ groups serves that purpose. However in polysaccharides like starch, guargum, xanthan gum etc. the large number of $-OH$ groups plays the metal ion coordination sites. Other polysaccharides like Sodium carboxylmethylated cellulose (CMC), Sodium alginate, Chitosan apart from $-OH$ groups $-COO^-$ (CMC and sodium alginate), $-NH_2$ groups (Chitosan) are present. These functional groups play an important role for binding the metal ions.

Thus if the metal ions attraction capabilities of both the natural polysaccharide and the synthetic polymers are combined it is possible to develop efficient low cost sorbents for the heavy metals. This can be done by grafting various synthetic polymeric chains of vinyl monomers into the various polysaccharides backbones. It was reported that dextan-g-polyacrylamide is a good remover of Fe^{+2}, Al^{+3}, Ni^{+2}, and Co^{+2} [10]. Some starch derivatives prepared by grafting of some water soluble synthetic polymers are studied by Khalil et. al for the absorption of various metal ions and shown that Hg^{+2} is absorbed selectively. Metal ion absorption studies of graft copolymer k-carrangeenan-g-N,N-dimethylacrylamide and CMC-g-N-vinylformamide were also studied by Behari et. al[11, 12].

Keeping this view in mind the present work was under taken (a) to achieve graft copolymerization of AM onto hydroxyl ethyl starch using ceric ammonium nitrate initiator (b) to investigate the metal ion removing capacity of the graft copolymer into different metal ions, Cu^{+2}, Fe^{+2}, and Ni^{+2} from their aqueous solution.

2. Experimental
2.1. Materials

Hydroxy ethyl starch (HES) was procured from Aldrich Chemical Company, USA. Acrylamide was procured from Loba Chemie, Mumbai. Ceric ammonium nitrate, Acetone and Sodium nitrate (analar grade) were procured from Loba Chemie, Mumbai India. Copper sulfate, Nickel chloride and Ferrous sulfate

were supplied by E.merck Ltd. Mumbai, India. Doubly distilled water was used for synthesis.

2.2. Synthesis

The graft copolymer of HES was synthesized using ceric ion induced redox initiation method[13]. A typical experimental detail is as follows: 2 gm of HES were dissolved in 100 ml of distilled water at the temperature 90^oC with constant stirring and bubbling of nitrogen for about 15 min. 10 gm of acrylamide was dissolved in 75 cc of distilled water and mixed with HES solution. The oxygen free nitrogen was purged through the solution for 20 min. At this stage 25 cc of CAN solution (0.1gm) was added to the reaction mixture followed by further purging with nitrogen for 10 min. The reaction was allowed to continue for 24 hours after which it was terminated by adding a saturated solution of hydroquinone. At the end of the reaction the polymer was precipitated by adding excess quantity of acetone. The precipitated polymer was then dried under vacuum. The homopolymer (PAM) is removed by solvent extraction technique using water as a solvent. Afterwards it was pulverized and sieved. The synthetic details are given in table-1

Table-1: Synthetic details of the graft copolymers

Polymer	Polysaccharide (gm)	Acrylamide (gm)	CAN Concentration (gm)	Percentage of conversion*	Intrinsic viscosity (η) (dL/gm)
HES-g-PAM	02	10	0.1	83.7	6.3

* Percentage conversion is calculated from the relation:
% conversion = [(wt of graft copolymer – wt of polysaccharide) / amount of acrylamide] x 100.

2.3. Intrinsic viscosity measurement

Intrinsic viscosity measurement of polymer solutions was carried out with the help of Ubbelhode viscometer (Constant: 0.00527) at 30^0C. The viscosity was measured in 1 M $NaNO_3$ solution. The intrinsic viscosity was calculated[14] by plotting on the same graph paper, $\eta_{sp/C}$ versus C and $\eta_{inh/C}$ Versus C; and then taking the common intercept at C = 0 of the best fitted straight lines through the two sets of points (as shown in Fig.-1). Here C is the polymer concentration in gm / dL. η_{sp} and η_{inh} are the specific and inherent viscosities respectively and are calculated from the following equations

$\eta_{sp} = (t-t_0) / t_0$. Where t is the time of flow of the solution and t_0 is the time of flow of solvent at the same temperature.

$\eta_{inh} = \ln \eta_r/C$. η_r is the relative viscosity which was calculated from the relation

$\eta_r = t / t_0$.

Fig-I: Intrinsic Viscosity measurement of HES-g-PAM
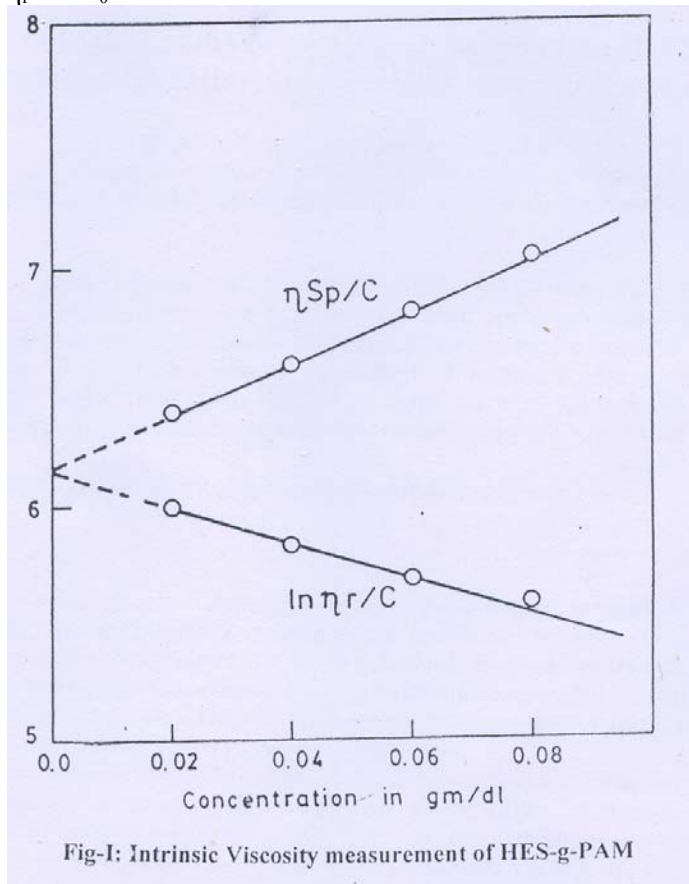
2.4. IR- Spectroscopy

The graft copolymer (HES-g-PAM) was subjected to IR-spectral analysis. A Perkin-Elmer-883 Infrared spectrophotometer (UK) was used and the potassium bromide (KBr) pellet method was followed for IR-study. The IR-spectrum of HES-g-PAM is shown in Fig -II.

2.5. Metal Ion Removal

Solution of (0.05 gm in 10 ml water) graft copolymer was added to 100 mL of metal ion solution of known concentration and then the mixture was stirred by a magnetic stirrer. The amount residual metal ions in the solution were determined by titration (complexometric) method. Metal ion removal capacity of the copolymer was calculated by using following relation[15].
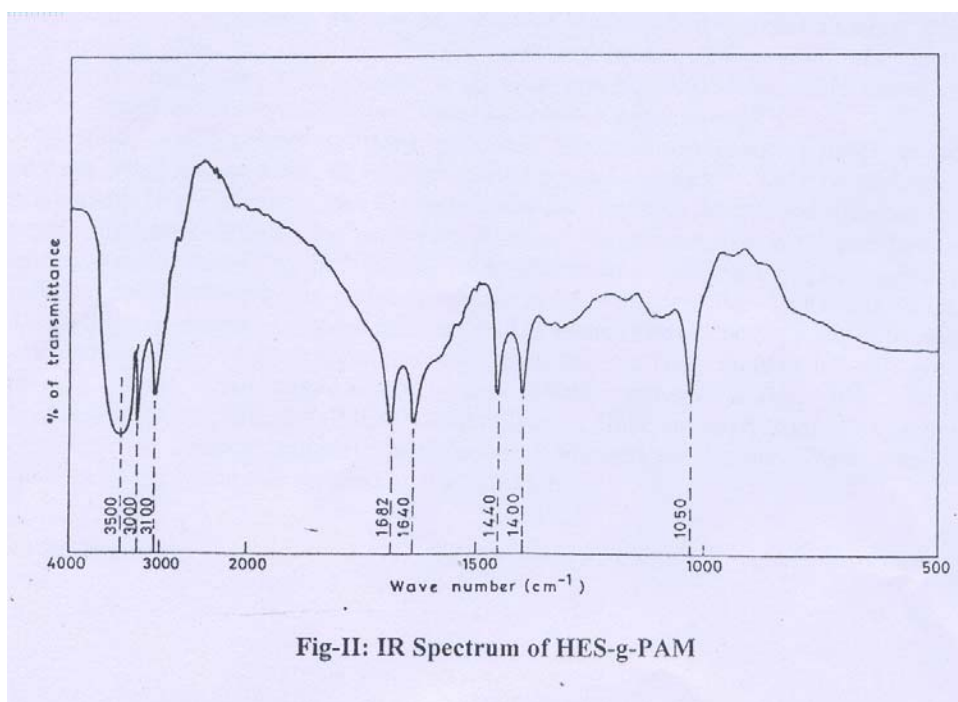
Fig-II: IR Spectrum of HES-g-PAM

$$\text{Metal ion removal capacity (mmole / gm of graft copolymer)} = \frac{(C_i - C_f) \times V}{M}$$

Where

C_i = Initial metal ion concentration in the solution (mmole / L)

C_f = Metal ion concentration in the solution after metal ion removal (m mole / liter).

V = Volume of the solution (liter)

M = The weight of the graft copolymer (gm)

The pH of the metal ion solution is kept constant at 5.0 since at higher pH the metal ions are precipitated as metal hydroxide[16]. Stock solution of copper ion was prepared by dissolving $CuSO_4$, that of nickel ion was prepared by dissolving $NiCl_2$ and solution of iron (II) ion was prepared by dissolving $FeSO_4$ in distilled water. The concentration of metal ion in solution was 4 mmole / liter in all three cases. The result is shown in Fig-III.

3. Results and Discussion
3.1. Synthesis

Graft copolymers based on hydroxyl ethyl starch have been synthesized by grafting acrylamide onto polysaccharide backbone by a radical polymerization

technique in aqueous medium using a ceric ion initiation method. Polymerization of just acrylamide was attempted using CAN, but it was observed that no polymer was formed, so it can be concluded that under the reaction conditions used in this investigation, the free radical was generated exclusively on the polysaccharide backbone. Hence homopolymer formation was minimized.

3.2. Proof of Grafting

The IR-spectrum is shown in Fig-II. From the spectrum it was found that the graft copolymer shows characteristic absorption on 1682 cm^{-1} which is for amide (>C=O) stretching , and 3100 and 3000 cm^{-1} for >N-H stretching (one for symmetrical stretch and the other for unsymmetrical stretching) and 1400 cm^{-1} is for C-N group, which indicate the presence of grafted polyacrylamide chains into the polysaccharide backbone.
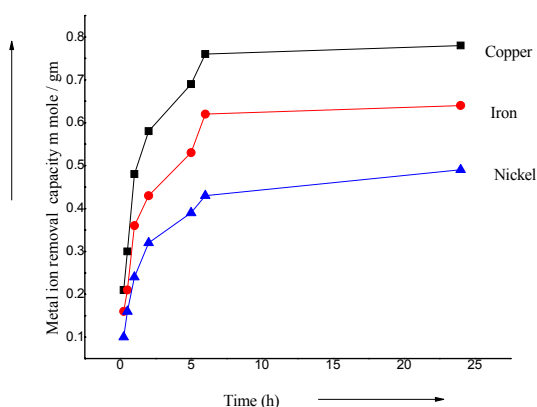
Fig-III: Metal ion removal capacity of HES-g-PAM

3.3. Metal Ion Removal

In this study HES-g-PAM was used for removal of three metal ions namely Cu^{+2}, Fe^{+2}, and Ni^{+2} from aqueous solution at pH 5.0. The result shows that metal ion removal capacity of the polymer is increased with increase in treatment time during 24 h. Metal ions are removed by the chelating with amide functional groups present in the graft copolymer. This requires an equilibrium condition. The absorption of metal ions increase with increasing treatment time to reach maximum value of the equilibrium state and then levels off. The absorption values depend on the metal ion used and follow the order $Cu^{+2} > Fe^{+2} > Ni^{+2}$ which indicates the stability of the complexes coordinating with nitrogen or oxygen of the amide group and the metal ions.

4. Conclusion

A high potential metal ion removing agent was obtained by the graft copolymerization of acrylamide onto hydroxyl ethyl starch. The spectroscopic data confirms that the grafting of polyacrylamide chains into the polysaccharide backbone occurs. Metal ion absorption capacity of graft copolymer increases with increasing treatment time. The absorption values of different metal ions on the hydroxy ethyl starch (HES) follow the order $Cu^{+2} > Fe^{+2} > Ni^{+2}$. Polyacrylamide grafted hydroxyl ethyl starch can be used as potential absorbent for the removal of ferrous and copper ions from polluted water.

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