Synthesis and Characterization of Sodium Carboxy Methyl Cellulose/Poly (Acrylamide) Magnetic Nano Composite Semi Ipn’s for Removal of Heavy Metal Ions

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Abstract: Sodium carboxy methyl cellulose (NaCMC)/poly(acrylamide) cross linked with N,N-methylene bisacrylamide semi IPN hydrogels were prepared using redox polymerization technique. These hydrogels are used for the preparation of nano composite hydrogels with magnetic properties which were further utilized for the removal of toxic metal ions. Semi IPN hydrogels were characterized by Fourier transforms infrared spectroscopy (FTIR), thermo gravimetric analysis (TGA) and scanning electron microscopy (SEM). Magnetic properties of hydrogels were characterized by vibration sample magnetometer (VSM). Swelling studies performed in water have been analyzed with the help of an empirical equation to investigate the diffusion mechanism. The sorption behavior with respect to contact time, initial pH, initial metal ion concentration, was investigated to determine the optimum sorption conditions. The adsorption capacities of Cu^{2+} and Ni^{2+} on the semi IPN gels and magnetic nano composite semi IPN’s were 0.74, 0.88 mM/g and 0.44, 0.58 mM/g, respectively. Desorption studies were also performed in acid media and EDTA, to observe whether the gels can be used as reusable tool for the metal ion removal. Compared to pure hydrogels the composite hydrogels are superior properties for removal of toxic metal ions.

Key words:

INTRODUCTION

Heavy metal ions pollution is one of the greatest problems causing threat to world environment due to rapid global industrialization and the increase in the world pollution. Metal ions such as Cd, Hg, Cu, Ni and Pb etc., which are commonly associated pollutants produce toxicity problems to humans because of their insusceptibility to biological degradation. They can specifically bind to proteins, nucleic acid and small metabolites in living organisms inhibiting their functions. [1, 2]. A number of methods have developed for the removal of these metal ions from waste waters [3-6]. Each method has its own draw back in terms of efficiency, cost and complexity.

Interpenetrating polymer networks (IPNs) are three dimensional networks which contain two or more homo polymers; these are natural or synthetic materials. IPN based hydrogels are three dimensional, hydrophilic, polymeric networks that can absorb up to thousands of times their dry weight in water or biological fluids [9, 10]. Semi IPN’s are a class of IPN’s which have a wide range of applications in biotechnology, drug delivery, pervaporation and separation and purification processes [7, 8]. Hydrogels are advantageous for many applications due to biocompatibility, which can be partially attributed to their soft, flexible nature and high water content.

Magnetic hydrogels are potentially attractive to the development of other technologies such as biomedical, nanometers, sensors, robot-like soft actuators and a variety of separation devices. Recently, magnetic separation has become a promising method for environmental purification as it is easily separated from the medium under applied magnetic field [11-14]. Hence, hydrogels with magnetic properties have become interesting adsorbents for the removal of toxic metals from the aquatic media [15]. Magnetic iron oxide in various forms have been used for treatment of radioactive and...
heavy metals from water and wastewater solutions [16, 17]. For example iron ferrite supported and used in a column mode in the presence of an external magnetic field has an enhanced capacity removal of contaminants in various forms from water. In previous studies poly (acrylamide) based hydrogels and composite hydrogels were used for separation of heavy metal ions [18].

Biopolymers like cellulose and their structural modification have been used as adsorbents for hazardous metals or strategically important metals in recent years. They are capable of lowering heavy metal ion concentrations to part per billion concentrations. Sodium carboxy methylcellulose contains many carboxylate ions so it can be anticipated as a pH sensitive fashion. In the present study NaCMC/Poly (acrylamide) semi IPN magnetic nanocomposite hydrogels (MNHs) have been prepared and used for separation of metal ions Cu\(^{2+}\) and Ni\(^{2+}\).

**MATERIALS AND METHODS**

**Materials**: Sodium carboxymethyl cellulose with high viscosity grade (500–800 cPs), acrylamide (Am), N,N-methylene bis acrylamide (MBA), potassium persulphate (KPS), were purchased from s.d fine chemicals, Mumbai, India. N,N,N’,N’-tetramethyl ethylenediamine (TEMED) from Aldrich (Germany), Iron (II) chloride tetrahydrate (FeCl\(_2\).4H\(_2\)O) and iron (III) chloride hexahydrate (FeCl\(_3\).6H\(_2\)O) were purchased from Merck (Mumbai, India). All the chemicals were used without further purification. Throughout the experiment double distilled water was used. Cu\(^{2+}\) and Ni\(^{2+}\) solutions were prepared by dissolving accurately weighed appropriate amounts of copper nitrate [Cu(NO\(_3\))\(_2\).3H\(_2\)O] and nickel ammonium sulphate [NiSO\(_4\)(NH\(_4\))\(_2\)SO\(_4\).6H\(_2\)O] in double distilled water to obtain solutions in the concentration range of 0.2-2.5 mM.

**Synthesis of Semi IPN Hydrogels**: Semi IPN hydrogels were prepared using free radical redox polymerization technique. Briefly 2 gms of acrylamide was dissolved in water after different amounts of NaCMC were added. To this mixture MBA, KPS and TEMED were added the polymerization was allowed to proceed at 37°C for 2 h. The hydrogels were obtained and then immersed in water for 2 days by changing the water for every 12 hr in order to remove the residual unreacted monomers and the solution fraction of the polymer. The resulting swollen gels were dried in air for 2 days and then in a vacuum oven until constant weight were attained at 40°C.

**Preparation of Semi IPN MNHs**: Magnetic particles were prepared inside hydrogel matrices by two steps. Firstly, semi IPN hydrogels were immersed in Fe (II) and Fe (III) ion aqueous solution (Fe (II): Fe (III) molar ratio is 1:2) for 12 h for loading. Secondly, the hydrogels were soaked in water to remove unbound and/or physisorbed metal ions for another 12 h. After cleaning, iron ions (Fe (II) and Fe (III)), metal ion loaded hydrogels were transferred into 30% ammonia solution for 6 h, magnetic nanoparticles were formed inside the hydrogels. Finally, the hydrogels were cleaned by washing with distilled water and dried in a vacuum oven at 40°C. The formations of magnetic composite hydrogels are shown in Figure 1 and 2, the chemical structure of semi IPN is presented at scheme 1.

Fig. 1: Photograph of representation of formation of Fe\(_2\)O\(_4\) magnetic nanoparticles present in the hydrogel network

Fig. 2: Attraction of magnetic hydrogels through magnetic bead
Scheme 1. Schematic representation of Semi IPN hydrogels

**Swelling Studies of Semi IPN MNHs:** Swelling experiments for the semi IPN and magnetic semi IPN hydrogels were carried out in water by mass measurements at 30°C. Known amount of dry hydrogels were soaked in water at different time intervals; the swollen hydrogels were taken out and blotted carefully to remove the surface-adhered water. The percentage of swelling ratio (%SR) and equilibrium swelling ratio (%ESR) were calculated using the following equations.

\[
\%SR = \left( \frac{W_e - W_d}{W_d} \right) \times 100
\]

\[
\%ESR = \left( \frac{W_e - W_d}{W_e} \right) \times 100
\]

where, \(W_i\) is the weight of swollen gel at time \(t\), \(W_e\) is the weight of the gel after establishment of equilibrium in the water and \(W_d\) is the dry weight of the hydrogels.

**Metal Ion Absorption Studies:** The experiments were carried out by placing weighed circular discs of hydrogels in 20 mL of 2 mM metal ion solution. After 1 hr they were removed from the solution. Initial and equilibrium concentrations were calculated from the measured absorbance values using UV spectrophotometer. The equilibrium adsorption amount, \(Q_e\) (mM/g-dry gel) was determined as follows.

\[
Q_e = \left( C_i - C_f \right) \frac{V}{M}
\]

Where, \(C_i\) is the initial concentration of the metal ion solution (mM L\(^{-1}\)), \(V\) is the volume of the solution used for the adsorption (L), \(M\) is the mass of the dry hydrogel (g) and \(C_f\) is the concentration of the ions remaining in solution.
Characterization of Hydrogels: Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer, Germany) analysis was performed to identify the chemical structure of the semi IPN and magnetic semi IPN hydrogels. The dry hydrogels (coated with a thin layer of palladium gold alloy) were studied for morphological variations by using a Carl Zeiss, EVO MA 15 scanning electron microscope. The grafting and thermal stability of the above membranes were given by TGA studies (TA instruments, Model: STA, Q600, USA).

The magnetization and hysteresis loop were measured at room temperature using a Vibrating Sample Magnetometer (Model 7300 VSM system, Lake Shore Cryotronic, Inc. Westerville OH, USA).

RESULTS AND DISCUSSIONS

FTIR Studies: The FTIR spectra of poly (acrylamide), semi IPN and magnetic composite semi IPN hydrogels crosslinked with MBA are shown in Figure 3. In the semi IPN MNHs (b and c) the broad peak appeared in the region of 3500-3000 cm\(^{-1}\) corresponding to the N-H stretching vibrations which are overlapped with –OH groups present in the NaCMC. Absorption bands at 2929 cm\(^{-1}\) corresponds to -CH stretching vibrations. The presence of strong absorption band at about 1619 cm\(^{-1}\) confirms the presence of carboxylate anion (COO\(^-\)), this peak overlaps with amide C=O peak. The bands around 1416 and 1325 cm\(^{-1}\) are assigned to -CH\(_2\) scissoring and –OH bending vibration respectively. The peak appeared at 1090 cm\(^{-1}\) is due to stretching vibrations of ether (C-O) group of NaCMC but it is not present in the poly (acrylamide) spectra. These are evidence for the formation of semi IPN hydrogel. But in the case of magnetic composite semi IPN hydrogel (c), the additional peak appeared at 590 cm\(^{-1}\) (Fe-O) corresponds to the formation of Fe\(_2\)O\(_3\) magnetic nano particles.

Scanning Electron Microscopy (SEM): The SEM images of semi IPN and magnetic composite semi IPN hydrogels are shown in Figures 4a & 4b. It can be seen that the hydrogel have porous network structure. But in the case of HGMNCs, clear formation of nanostructures was found all over the hydrogel However, these are only bulk iron oxide nano particles can be clearly seen in SEM image of HGMNCs. From these images the size of each individual iron oxide nano particles was calculated and found to have a size of ~ 24 nm.

Fig. 3: FT-IR spectra of poly acrylamidehydrogel (a), semi IPN hydrogel (b), magnetic nanocomposite semi IPN ©

Fig. 4: SEM pictures of semi IPN hydrogels (a), magnetic nanocomposite semi IPN (b)
Thermo Gravimetric Analysis: The semi IPN and its magnetic composite semi IPN hydrogels were characterized by thermo gravimetric analysis shown in Figure 5. TGA is important for determination of percentage of weight loss of hydrogel as well as composite hydrogel matrix. The starting decomposition temperature of hydrogel is 201°C which is higher than that of the hydrogel magnetic nanocomposite (196°C) [19]. This observation is due to the catalytic property of the Fe$_3$O$_4$. The final decomposing temperature of hydrogel decreased compared to magnetic nanocomposite hydrogel. The difference in decomposition between the hydrogel and magnetic composite hydrogel is found to be 8% and illustrates the presence of Fe$_3$O$_4$ magnetic nanoparticles present in the hydrogel networks.

Magnetic Properties of Semi IPN MNHs: Iron oxide nanocomposites have to exhibit super paramagnetic properties which can be established by measuring their magnetic saturation using magnetometer (VSM). The magnetization loops (magnetization versus applied field (B-H)) of semi IPN hydrogel magnetic nanocomposite. The variation in their magnetic moments of the prepared hydrogel magnetic nanocomposites was investigated as a function of varying the magnetic field in the range of -15000 to 15000 Oe. The saturation magnetization (Ms) and coercivity (Hc) for the semi IPN hydrogel magnetic nanocomposite was found to be 8.9 emu/g and 14731 Oe. This Ms value is far below compared to pure magnetic nanoparticles (Fe$_3$O$_4$) (66.1 emu/g). But this value is expected because the presence of only ~14.5% of magnetic nanoparticles in the hydrogel (theoretical Ms 9.254 emu/g, experimental 9.3 emu/g). Therefore, a single domain of magnetic nanoparticles formed within the hydrogel networks exhibit a unique phenomenon of super paramagnetism [20].

Swelling Studies: The results of swelling studies of different amounts of NaCMC are shown in Figures 6a and 6b. Compared to pure poly AAm hydrogel the swelling ratio of semi IPNs increase. The increase in swelling capacity can be explained increase the amount of NaCMC. To determine the nature of water diffusion into hydrogels, initial swelling data were fitted to the following exponential equation [18].
Table 1: Swelling kinetics parameters of different formulations.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>% of NaCMC</th>
<th>AAm (g)</th>
<th>% Equilibrium swelling studies</th>
<th>n</th>
<th>k</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semi IPN-1</td>
<td>0</td>
<td>2</td>
<td>904</td>
<td>0.5501</td>
<td>0.019249</td>
<td>0.9996</td>
</tr>
<tr>
<td>Semi IPN-2</td>
<td>1</td>
<td>2</td>
<td>1307</td>
<td>0.5739</td>
<td>0.017985</td>
<td>0.9981</td>
</tr>
<tr>
<td>Semi IPN-3</td>
<td>2</td>
<td>2</td>
<td>1470</td>
<td>0.5463</td>
<td>0.023089</td>
<td>0.9986</td>
</tr>
<tr>
<td>Semi IPN-4</td>
<td>3</td>
<td>2</td>
<td>1977</td>
<td>0.6169</td>
<td>0.01845</td>
<td>0.9994</td>
</tr>
<tr>
<td>Semi IPN-4M</td>
<td>3</td>
<td>2</td>
<td>1453</td>
<td>0.6387</td>
<td>0.014598</td>
<td>0.9982</td>
</tr>
</tbody>
</table>

where $M_t$ and $M_e$ represent the amount of water absorbed by the hydrogels at time $t$ and at equilibrium, $k$ is a characteristic constant of the hydrogels and $n$ is a characteristic exponent of the mode of transport of the penetrant. These results are shown in Table. I. For the first case, if $n < 0.45$, corresponding to Fickian diffusion, in this case the water molecules are considered to diffuse through the polymer networks simply through process of diffusion. The second case corresponds to non-Fickian diffusion with $n$ values are $0.45 \leq n \leq 0.89$. In this case the diffusion mechanism is characterized by two processes occurring simultaneously-diffusion through the pores and macromolecular relaxation of the hydrogel network. In the third case, for $n > 0.89$, the diffusion mechanism of water is exclusively governed by macromolecular relaxation, i.e. super case II. In the Present study, $n$ values for the hydrogels were approximately between 0.55 to 0.65, indicating non-Fickian diffusion, with tendency towards macromolecular relaxation. Compared to pure hydrogels magnetic nanoparticles loaded hydrogels the $n$ value increased due to magnetic nanoparticles loaded hydrogels may increase the crosslink density and consequently hinder the diffusion through pores [19].

**Effect of pH on Swelling:** The swelling behavior of Poly(NIPA-co-APA) SRsemi IPN MNHs was observed as pH dependent due to the ionization/deionization of the ionisable functional groups, such as -NH$_2$ or -COO$^-$ (Figure 7). At lower pH values, these groups do not ionize and keep the network at its collapse state. At higher pH values, these groups ionize and their charges repel each other, resulting in the swelling of the hydrogel network.

**Effect of pH on Metal Ion Adsorption Studies:** The ionisable functional groups, such as -NH$_2$ or -COO$^-$, on the surface of hydrogels, may gain or lose a proton, resulting in a surface charge that varies with pH (Figure 8). At low pH, surface sites are protonated and the surface becomes positively charged, while at high pH the ionisable groups lose their protons and the surface becomes negatively charged. The pH value in aqueous solution is a very critical parameter affecting both the removal capacity and the removal mechanism of Cu$^{2+}$
and Ni\(^{2+}\) ions. As pH value increases (pH 2-5) its removal capacity of Cu\(^{2+}\) and Ni\(^{2+}\) by uptake also increases. In alkaline conditions, complete sorption was observed, but in this pH region the metal ion removal originates from precipitation of hydroxides rather than from sorption. The ability of a material to capture metals is controlled in part by the number of available functional groups used for binding metals.

**Effect of Initial Concentration on Metal Ion Adsorption Studies:** Figure 9 shows the relationship between initial metal ion concentration and the adsorbed amount. It is clear from the figure, the adsorption amount of metal ions increased with increasing initial ion concentration then reached a plateau value at higher concentration due to the saturation of the chelating sites of the hydrogels. The adsorption is measured for Cu\(^{2+}\) and for Ni\(^{2+}\) at pH 5 and 4 respectively. The maximum adsorption capacities of the hydrogels was found to be 0.74, 0.88 mM/g for Cu\(^{2+}\) and 0.44,0.5 mM/g for Ni\(^{2+}\) respectively. These high adsorption efficiencies were attributed to hydrophilic nature of polymer matrix due to the presence of hydroxyl (-OH), amine (-NH-) and carboxyl (-COO) groups, which had an adequate affinity to the metal ions.

**Adsorption Isotherm:** The equilibrium data were better fitted to Langmuir adsorption isotherm model. The analysis of adsorption data is important for developing an equation that accurately represents the results and that could be used for design purposes. The most widely used isotherm equation for modeling equilibrium is the Langmuir equation. In this study, we attempted to analyze adsorption at different concentrations (0.2-2.5Mm) by this model.

$$\frac{1}{Q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0C_e}$$

where, Q\(_e\) is the amount of metal adsorbed per unit weight of the sorbent (mg/g) and Q\(^0\) and b are Langmuir constants indicating the maximum adsorption capacity and energy of adsorption, respectively. The linear plot of 1/C\(_e\) versus 1/Q\(_e\) with high correlation coefficient (r\(^2\) >0.9 ) values, indicate the applicability of Langmuir isotherm. The values of Q\(^0\) and b were determined from the slope and intercept of linear plots and are presented in Table 2. The values of Q\(^0\) for Cu\(^{2+}\) and for Ni\(^{2+}\) are 0.74, 0.88 mM/g and 0.44, 0.5 mM/g for pristine and MNC hydrogels respectively. The values of Langmuir constants, correlation coefficient, r\(^2\) are given in Table 2. Values of r\(^2\) less than unity indicates favourable adsorption. Q\(^0\) value is higher for MNC compared with pristine hydrogels, thus indicating better adsorption. Values of Q\(^0\) are significantly higher for Ni\(^{2+}\) compared with Cu\(^{2+}\) in all the kinds of gels. A large value of b also implied strong binding of Ni\(^{2+}\)to the gels. The Langmuir model fitted better with the experimental data (Figure 9) rather than the Freundlich model.

**Effect of Contact Time:** Since, the adsorption process is a transfer of the pollutant from the liquid to the solid phase, the contacting time between the two phases has an effect on the mass transfer rate. Figure 10. shows the

Table 2: Langmuir parameters with regression analysis of copper and nickel sorption on Nacmc gels

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Gels</th>
<th>Q(^0) (mM g(_i))</th>
<th>b (L/mg)</th>
<th>r(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^{2+})</td>
<td>SIPN</td>
<td>0.74</td>
<td>0.015</td>
<td>0.979</td>
</tr>
<tr>
<td></td>
<td>MNC</td>
<td>0.88</td>
<td>0.031</td>
<td>0.9927</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>SIPN</td>
<td>0.44</td>
<td>0.018</td>
<td>0.9725</td>
</tr>
<tr>
<td></td>
<td>MNC</td>
<td>0.58</td>
<td>0.035</td>
<td>0.9984</td>
</tr>
</tbody>
</table>
kinetics of adsorption expressed as the adsorbed quantity of copper and nickel over one gram of solid support. It is evident from the figure that adsorption was rapid initially and became slower with lapse of time. At the initial stage the process of adsorption was fast due to the availability of abundant free sites near the surface where there is less hindrance for the approaching metal ions. Evidently MNHs has higher sorption ability for the uptake of Cu$^{2+}$ and Ni$^{2+}$ than the pristine hydrogels with respect to contact time all the materials reached saturation after 60 minutes.

**Desorption Studies:** Desorption of Cu$^{2+}$ and Ni$^{2+}$ from gels was studied with HCl and EDTA as regenerants. When 0.01M HCl or EDTA were used desorption was only 60$\%$ and 72$\%$ respectively of adsorbed ions on membranes in to the solutions. As the concentration of the regenerant is increased to 0.1M the desorption of ions increases to 80$\%$ and 94$\%$ for HCl and EDTA respectively.

When acid is used as a regenerant, the amine or carboxyl (-OOC) groups of the sorbents get protonated and this induced the repulsive force between the adsorbed metal ions and the sorbent. Hence Cu$^{2+}$ and Ni$^{2+}$ are released into the solution. However, when the complexing agent, EDTA is used as a regenerant, it showed a strong affinity for the adsorbed Cu$^{2+}$ and Ni$^{2+}$ Thus the metal ions are released into solution in the form of a soluble Cu$^{2+}$ and Ni$^{2+}$ - EDTA Complex.

**Reusability:** The cycle of extraction-recovery-regeneration was repeated thrice. The uptake performance of regenerated sorbent was found to be close to the freshly prepared sorbents which indicate that the sorbents can be regenerated and reused respectively at least for three times.

**CONCLUSIONS**

Semi IPN Hydrogel magnetite nanocomposite were prepared by a very simple and effectively by in situ method, which involved developing of magnetite nanoparticles in a polyacrylamide/NaCMC hydrogel. The formation of semi IPN and magnetite nanoparticles and their magnetic properties were confirmed using Fourier transform infrared spectroscopy. HMNCs had a lower thermal stability at the initial decomposition temperature and higher thermal stability at the final decomposition temperature. The average size of magnetic nanoparticles was confirmed by transmission electron microscopy. The resulting magnetic nanoparticles were able to successfully separate Cu$^{2+}$ and Ni$^{2+}$ metal ions from aqueous solutions.

**ACKNOWLEDGEMENTS**

Authors highly thankful to BRNS project (Grant No.: 2010/37C/53BRNS/2538, Dated 23-02-2011), BARC, Mumbai, India.
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