Removal of Selective Metal Ions from Water with Hydroxy Propyl Cellulose Hydrogel

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In this study, environmentally friendly hydrogels prepared from hydroxy propyl cellulose hydrogels blended with poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP) were employed to absorb selected metal ions of Cu and Fe to find potential applications in removal of metal ion from water or in wastewater treatment. Highest adsorption capacity of hydroxy propyl cellulose hydrogels blended with PVA or PVP is shown at 0.04 % (w/v) of the metal ion solutions. Hydroxy propyl cellulose hydrogel when blended PVA has shown greater adsorption of Fe(III) ion than Cu(II) ion at higher pH. Hydroxy propyl cellulose hydrogel when blended with PVP also showed maximum adsorption capacity rather than PVA blended hydrogel.

Keywords: Hydroxy propyl cellulose, Hydrogel, Poly(vinyl alcohol), poly(vinyl pyrrolidone), Swelling ratio.

INTRODUCTION

Hydrogels are multicomponent systems having three dimensional chemically cross-linked polymer networks able to swell in water increasing substantially their original volume while maintaining integrity [1]. It has been recognized that hydrogels are promising materials for the removal of heavy metal ions [2] after facilitating incorporation of different chelating groups into the polymeric network [3]. It is a fact that charged hydrogels which are functionalized by carboxylic acid, amine, hydroxyls or sulphonic acid groups can form complexes as good poly-chelatogens [4] with toxic metal ions of Cd, Pd, Cu, Hg, *etc.* so as to remove from the aqueous solutions [5]. Removal of toxic metal ions from wastewater by developing novel sorbents of hydrogels opens a new front of research field and shifts from highly expensive processes like ion exchange, reverse osmosis, *etc.* to readily available low cost ones which do not even need electrical components during the last years. It is also fact that the development of hydrogel adsorbents must satisfy certain criteria like specific, fast complexation and reusability [6]. Hydrogel based adsorbents have interesting features due to their high hydrophilicity, biocompatibility, non-toxicity and biodegradability. Super-absorbent hydrogels have also been used in agriculture, pharmaceuticals and medicals items, disposal diaper, *etc.* [7].

Bekiari *et al.* [5] have reported the use of poly sodium acrylate (PANa) hydrogels for the removal of crystal violet and Cu^{2+} from water and found that PANa hydrogel adsorb stronger Cu^{2+} ions due to complex formation between the hydrogel and the metal ions by engaging one metal ion per two carboxylate anion than crystal violet just due to electrostatic interaction. The removal of metal ions like Fe(III), Cu(II) and Mn(II) was also found to depend on treatment time, pH of the medium, initial feed concentration of the metal ion [5,6]. Further, to the best of our knowledge the interaction of metal ion with hydroxy propyl cellulose (HPC) hydrogel is rather less nor available during literature survey. In the light of the above facts, an attempt is made to investigate the potential applicability of using HPC hydrogel blended with poly(vinyl alcohol) (PVA) or poly(vinyl pyrrolidone) (PVP) in the extraction of metal ions from water using the interacting behaviour of metal ions with hydrogels.

EXPERIMENTAL

The non-ionic polymers *viz.*, hydroxypropyl cellulose (HPC), poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone)

(PVP) were obtained from Hi-media extra pure. The surfactant sodium dodecyl sulphate (SDS, an anionic surfactant) was also procured from Hi-media. The polymers as well as the surfactants and other samples employed in this study were used without further treatment.

Preparation of solution: All the solutions were prepared by dissolving a known weight of solute in a known volume of the solvent. Stock solution of surfactant was prepared by dissolving a weighed amount of surfactant in a known volume of double distilled water having a conductivity of less than 2 μS. For example, a standard stock solution of anionic surfactant SDS was prepared by dissolving 2.9 g of the sample in a 100 mL volumetric flask. The concentration of SDS solution was determined by titrating against a standard (100 mM) solution of cationic surfactant hyamine using methylene blue as indicator. Stock solutions of about 10 % w/v each for HPC, PVA and PVP were prepared by dissolving weighed amount of polymer in 100 mL volumetric flask. The dissolution was carried out by standing the solutions for about 48 h at 25 ºC to ensure a clear solution. Other solutions of lower concentrations of the mixture were prepared by dilution method.

Preparation of HPC hydrogels: About 10 mL of HPC 10 % (w/v) stock aqueous solution was mixed with 3 mL of 3 % (w/v) borax solution and the mixture was warmed briefly for about 10 min to ensure uniformity. The mixture was then slowly cooled to room temperature and kept at the same temperature for one night to eliminate air bubbles when borax cross-linked gel was obtained. Then 5 mL for each 2 % (w/V) PVA polymer and 2 % (w/v) PVP polymer were added with constant stirring to prepare HPC blended hydrogel and left the mixture for about 48 h at 25 ºC to remove air bubble. The mixture was briefly warmed and kept overnight after which a uniform simple HPC and HPC blended PVA and PVP were obtained.

Swelling ratio: The swelling ratio of HPC and HPC blended hydrogels of PVA and PVP with borax were measured gravimetrically both in presence and absence of SDS surfactant. The hydrogel samples were incubated in buffer solution of pH 2, 4 and 7 at 30 ºC for at least 2 h. By recording the weight of a cut piece of gel before and after ageing, swelling ratio was calculated [8] with the symbols having their usual meanings from the following eqn.:

$$\text{Swelling ratio} = \frac{W_s - W_o}{W_o} \times 100 \qquad (1)$$

pH: The pH of the solution in which hydrogel were supposed to measure swelling ratio both in presence and absence of surfactant was monitored using the CyberScan Series PC 5500 (Eutech Instruments) bench meter which operates with a state of art touch screen capable of measuring pH, conductivity and ions. The measurements were used to record the changes in pH values with relative accuracy of ± 0.002. Temperature of the solution/gel during experiments was maintained by circulating thermostated water.

Adsorption: The amount of adsorption of metal ions by hydrogels is studied [8] using the following eqn:

$$\text{Adsorption} = \frac{V(C_1 - C_2)}{W} \qquad (2)$$

where, V is the volume of the solution, W is the weight of hydrogel (g), C_1 and C_2 are the concentrations of metal ions before

and after the adsorption by dipping hydrogel in solution for about 4 h. All tested samples were recorded in triplicate.

Spectroscopic analysis: The concentration of metal ion solution before and after dipping the hydrogel in metal ion solution was monitored with the help of UV-visible scanning spectrophotometer (Shimadzu UV-2456) in the wave length range from 300 to 800 nm at 30 ºC. The temperature of solution was maintained constant by circulating thermostated water around the sample solution.

RESULTS AND DISCUSSION

The swelling behaviour of HPC-borax hydrogel is measured as a function of time (in min) at different pHs of 2, 4 and 7 at room temperature around 30 ºC. The behaviour is observed to be highest for hydrogel at pH = 7 and lowest at pH = 2 (Fig. 1). This is attributed due to the higher degree of association or matrix formation between polymers and the cross-linker borax at pH 7, which means that less available space for water to move freely inside the network and thus increases the swelling ratio at high pH value.
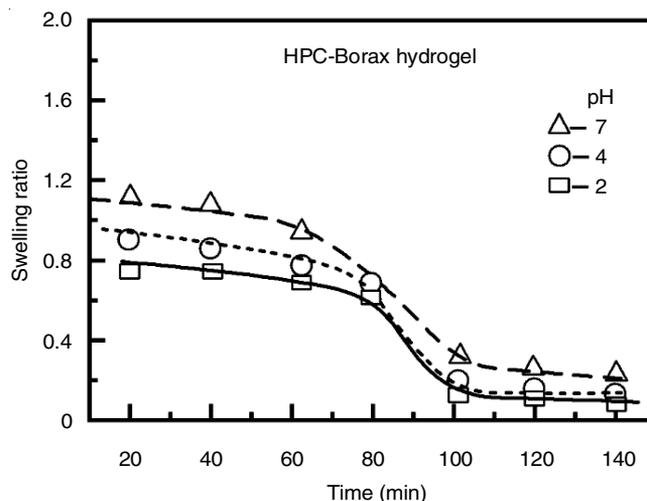
Fig. 1. Swelling ratio of HPC-Borax hydrogel as a function of time at different pH's

In Fig. 2, presence of anionic surfactant SDS (4 mM) in HPC-borax hydrogel have shown maximum swelling ratio at pH 7. Lowest swelling ratio of hydrogel in same pH environment was observed at higher surfactant concentration (12 mM). These observations are explained as the surfactant when present as monomer facilitates the cross-linking network of hydrogel due to destabilization effect occurred because of the electrostatic repulsion between negative charge of polymer chain and SDS monomers, thus leading to the expansion and mixed micelle formation in the system [4]. But at higher concentration *i.e.* at 12 mM of SDS, the surfactant micelles apparently start destabilizing the crosslinking in the gel network therefore resulting in the decrease of swelling ratio. The swelling ratio behaviour of HPC-Borax when blended with PVA or PVP in presence of SDS at pH 7 are shown in Figs. 3 and 4. It has been observed that introduction of either PVA or PVP along with SDS as monomer during the formation of HPC-borax hydrogel helps in further expansion of the gel network thereby making available more space so as to swell freely in water.
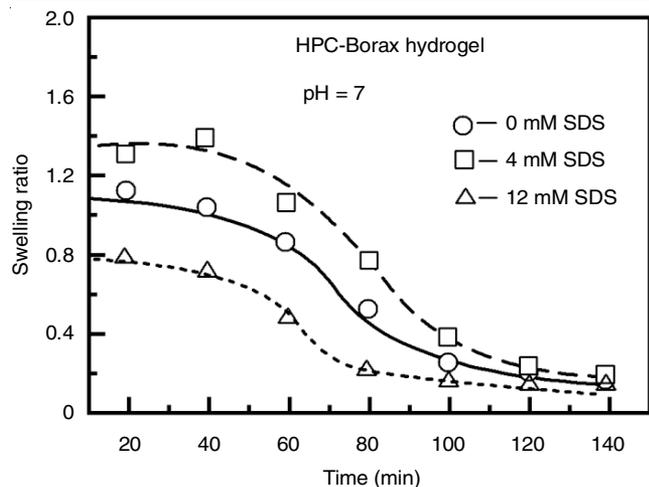
Fig. 2. Swelling ratio of HPC-Borax hydrogel in presence of SDS at pH = 7
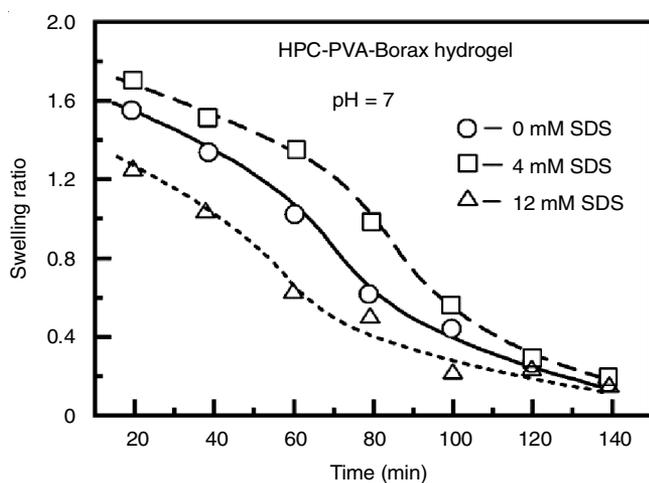
Fig. 3. Swelling ratio of HPC-PVA-Borax hydrogel in presence of SDS at pH = 7
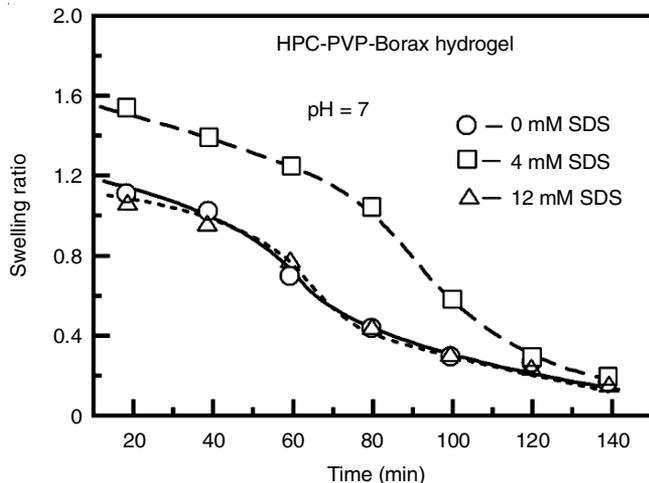
Fig. 4. Swelling ratio of HPC-PVP-Borax hydrogel in presence of SDS at pH = 7

However, the effect is greater for PVA than PVP suggesting for a possible availability of more space in case of PVA due to electrostatic repulsion [8,9]. It is further observed that the effect of SDS at higher concentration *i.e.*, in post-micellar region in both blended HPC-Borax hydrogel have not showed an appre-

ciable change in the swelling ratio behaviour but lower than hydrogel without SDS.

The absorption spectrum of aqueous $FeCl_3$ solution and $CuSO_4$ are recorded in Figs. 5 and 6 at pH 7 and observed that maximum absorptions for $FeCl_3$ and $CuSO_4$ at around 424 nm and 756 nm, respectively. A calibrated absorption curve for aqueous $FeCl_3$ solution at 424 nm for various concentrations is shown in Fig. 7. The curve shows a linear behavior as expected
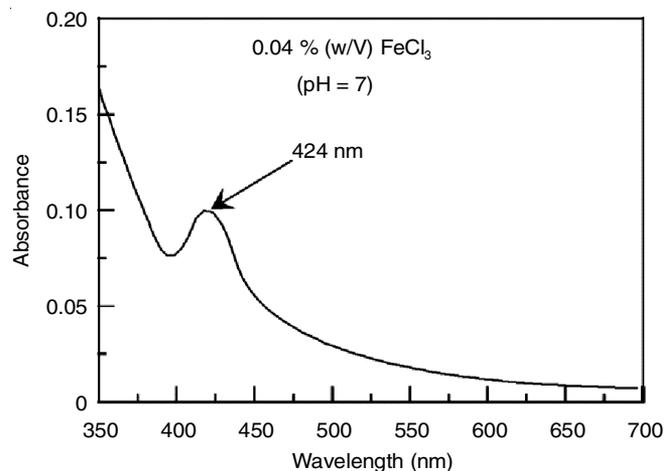
Fig. 5. Absorption spectra of 0.04 % (w/v) $FeCl_3$
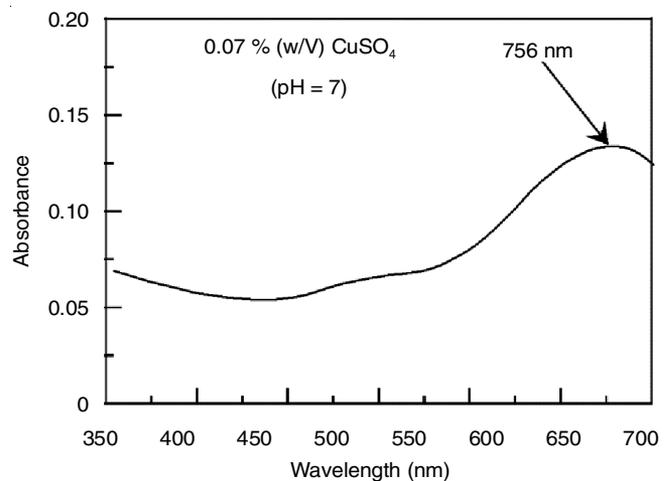
Fig. 6. Absorption spectra of 0.07 % (w/v) $CuSO_4$
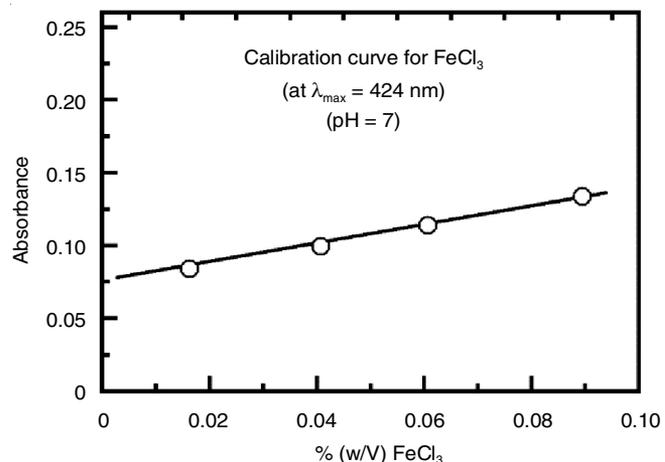
Fig. 7. Calibration curve of $FeCl_3$ solution at λ_{max} = 424 nm as a function of metal ion concentration

and established the relationship between absorbance values and the FeCl$_3$ concentration. A similar calibration absorption curve for aqueous CuSO$_4$ solution at 756 nm is also shown in Fig. 8. Using the calibration curves, the concentration of Fe(III) and Cu(II) ions solution were determined before and after dipping the hydrogel in solution for about 4 h.
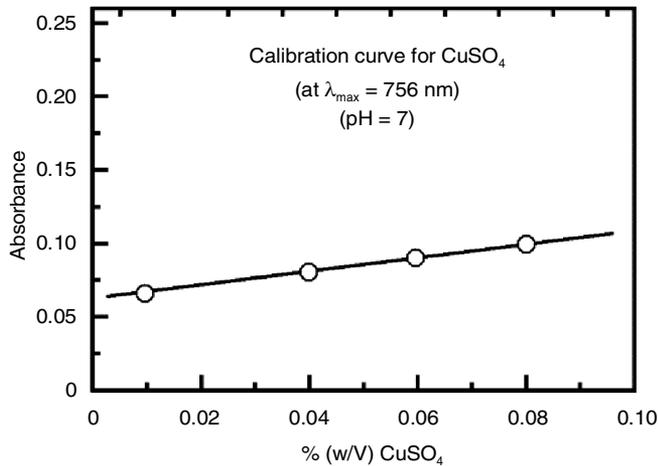
Fig. 8.   Calibration curve of CuSO$_4$ solution at λ_{max} = 756 nm as a function of metal ion concentration

The amount of adsorption or uptake of metal ion of CuSO$_4$ and FeCl$_3$ solutions by blended hydrogel were also calculated using eqn. 2. Figs. 9 and 10 have shown a maximum adsorption of metal ion solution by HPC-Borax hydrogel in presence of 4mM SDS when blended with polymers at pH 7. A maximum concentration of 0.04 % (w/v) for both the metal ion solutions is also observed after which it appear to stop further adsorption due to unavailability of the space for the metal ion in the gel matrix. Maximum adsorption of metal ion by PVP blended HPC-Borax hydrogel in presence of SDS monomer suggested the larger number of available sites to bind inside the gel matrix in comparison to PVA blended hydrogel. In the above mentioned environment, PVA blended hydrogel may have taken part more easily and extensively thereby making less binding sites in the gel matrix.
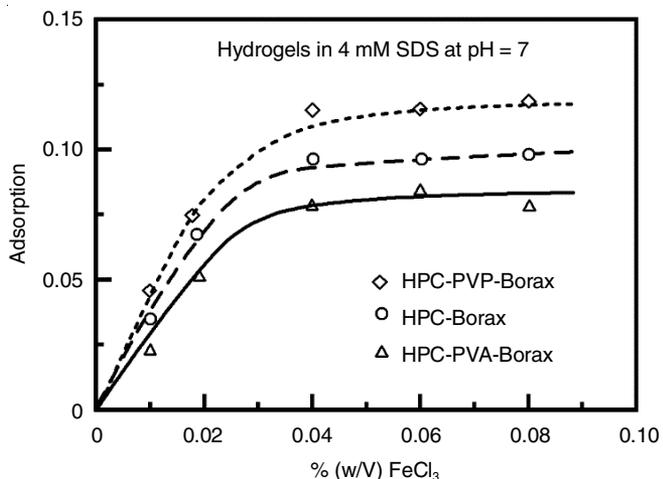
Fig. 9.   Adsorption of FeCl$_3$ by HPC-Borax hydrogel blended with PVP or PVA in presence of 4 mM SDS at different metal ion concentration
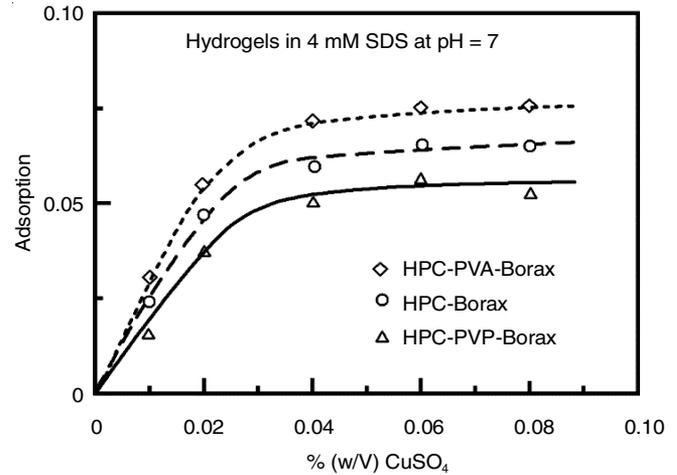
Fig. 10. Adsorption of CuSO$_4$ of HPC-Borax hydrogel blended with PVP or PVA in presence of 4 mM SDS at different metal ion concentration

The adsorption of Cu(II) and Fe(III) ions solution at (0.08 % w/v) on 2 g of PVP blended HPC-Borax hydrogels in presence of SDS monomer at 4 mM were compared at different pH's and is presented in Fig. 11. In the figure, it is seen that PVP blended HPC-Borax hydrogel have higher capacity of adsorption for Fe(III) than Cu(II) ion solution inside the hydrogel matrix in same pH environments. This is due to the fact that PVP blended HPC-Borax hydrogel becomes a polyelectrolyte hydrogel and therefore interaction between the hydrogel and of Fe(III) ion is stronger than Cu(II) ion as reported in case of carboxy methyl cellulose hydrogels with monovalent and divalent metal ions interaction [10]. The interaction between the -OH groups in hydrogel contributed from the polymers and the metal ions may have facilitates stability, and water insolubility of these polymeric matrices therefore resulting in increasing the interaction by increasing the crosslinking structure.
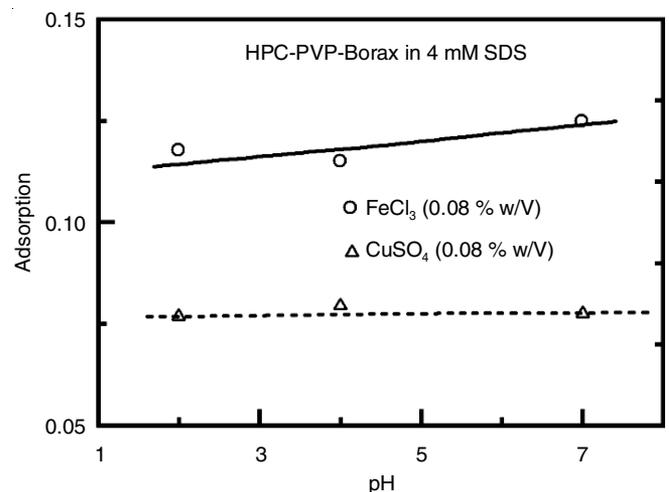
Fig. 11. A comparison for the adsorption of FeCl$_3$ and CuSO$_4$ solution by PVP blended HPC-Borax hydrogel at different pH

Conclusion

Hydroxy propyl cellulose-Borax hydrogel shows higher swelling ratio in high pH due to expansion and inter-hydrogen bonding inside the gel network when added with PVA than PVP in the presence of SDS surfactant. The PVA blended

hydrogel has a maximum capacity to adsorb upto 0.04% (w/v) of the metal ions and appears to be remained saturated even at higher concentration of the metal ion solution. The content of PVP in the gel network also found to be facilitated for adsorption onto HPC-gel network better than PVA. Fe(III) ion solution has shown higher interacting power with hydrogel than Cu(II) in the same environment.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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