

Removal of Synthetic dyes from water by using IPN hydrogels of chitosan incorporated acrylic acid and hydroxyl ethyl methacrylate copolymer

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Abstract

Several interpenetrating network (IPN) hydrogels were made by free radical *in situ* crosslink copolymerization of acrylic acid (AA) and hydroxy ethyl methacrylate (HEMA) in acidic solution of chitosan. N,N-methylene bis acrylamide (MBA) was used as comonomer crosslinker for making these crosslink hydrogels. These hydrogels were prepared by varying comonomer compositions, crosslinker%, initiator concentration and % of chitosan polymer in water. All of these hydrogels were characterized by FTIR, SEM, XRD and swelling parameters. These hydrogels were used for adsorption of two important synthetic dyes i.e. safranin-T (ST) and brilliant cresyl blue (BCB) from water.

Keywords:

Chitosan;
Crosslinker;
Dyes adsorption;
Hydrogel;
IPN.

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1. Introduction

The textile, polymer, paper, pharmaceutical and other chemical industries use synthetic dyes for coloring various products. Amongst the various synthetic dyes, safranin-T (ST) and brilliant cresyl blue (BCB) dyes are widely used in textile industries for dyeing cotton, silk and wool as well as in other industries. However, these dyes are hazardous [1, 2] and the presence of the low concentration of these dyes in water causes potential threat to human health. For the removal of these dyes from water functional hydrogels are used. The functional groups which are present in their structures show electrostatic interactions like hydrogen bonds with the dye molecules. Natural polymers which are present in huge amounts in nature are used to prepare functional hydrogels. These biopolymers are biodegradable and non toxic. Among the various biopolymers, chitin, a polysaccharide consisting of β -(1-4)-2-acetoamido-2-deoxy-d-glucose is the second most abundant polymer in nature after cellulose. Chitin is a naturally abundant mucopolysaccharide which is extracted from crustacean shells. These shells are the waste products of seafood processing industries. The deacetylation of chitin results in the formation of Chitosan (CS), a polyaminosaccharide which is also used as an effective adsorbent for heavy metal ions and dyes. The hydroxyl (-OH) groups present in chitosan shows electrostatic interaction with metal ions and dyes by means of hydrogen bonding. Thus, chitosan and its derivatives have been widely used as adsorbents [3]. The physical or chemical modification of chitosan is done to improve its adsorption properties as well as mechanical strength. Chemical crosslinking with glutaraldehyde, epichlorohydrin, ethylene glycol diglycidyl ether or isocyanates [4], results in the formation

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of semi and full interpenetrating network of chitosan with synthetic polymers [5] or composites of CS [3]. For the removal of metal ions or dyes from water, these modified CS have been used as adsorbents [3, 6].

Hydrogels are the crosslinked three-dimensional hydrophilic polymers. Crosslinking reduces their water solubility. They show extensive swelling in water and other similar solvents. The hydrogels allow the diffusion of dye molecules through the porous structure networks. The hydrophilic polar functional groups of these gels provide absorption and trapping of dyes from wastewater. Thus, the hydrogels may be used as an alternative adsorbent for the removal of dyes from aqueous solution. Various hydrogels were synthesized and their adsorption behavior for dyes was studied. The effects of pH value of the dye solution and adsorption temperature on the adsorption capacity of dye on the hydrogel have been investigated. Besides water, a hydrogel can also preferentially absorb low concentration of dissolved dye, metal ions, pesticides, other organic molecules etc. by chemical interactions.

The present work includes the synthesis of hydrogels from copolymer of acrylic acid and hydroxyethyl methacrylate with N, methylene bis acrylamide as crosslinker comonomer. Further, interpenetrating network (IPN) type hydrogels have also been synthesized by allowing copolymerization of AA and HEMA in the matrix of a acidic aqueous solution of natural polymer i.e. chitosan. By varying comonomer ratio, concentration of crosslinker, initiator and chitosan in water several hydrogel polymers have been synthesized. Also the characterizations of these hydrogels have done. The swelling properties of these hydrogels have been investigated in details. Some of these selected hydrogels have also been used for removal of low concentration of dyes from water.

Synthetic monomers such acrylamide, acrylic acid, hydroxyethyl methacrylate based Homo and copolymer hydrogels have been extensively used as adsorbents for dyes [7, 8, 9]. The objective of the present work was to combine the advantages of a natural and a synthetic polymer by making their stable composites. Crosslinked acrylic hydrogels have been used as pH responsive adsorbents. In the present treatise acrylic acid and hydroxyethylmethacrylate were copolymerized and crosslinked with MBA in aqueous solution of CS. For solution polymerization in water at least 10-15 wt% concentration of synthetic monomers in water is required [7] while it is difficult to make concentrated CS solution in water (in presence of acetic acid) because of its high viscosity. Thus, polymerizing synthetic comonomers in the matrix of CS by solution polymerization is difficult. Instead, low concentration of CS may be incorporated in the matrix of crosslink copolymer to form CS filled composite. In the present work these CS filled copolymer composites were used for removal of two important industrial dyes viz. safranin-T (ST) and brilliant cresyl blue (BCB) dye from water. These dyes are widely used for coloring plastics and textiles. The peculiarities are that, both of these aromatic dyes are not biodegradable but highly soluble in water. Removal of low concentration of these dyes from water by using a low cost biopolymer based adsorbent would be very effective. Thus, in the present work CS incorporated copolymer gels have been used for removal of these two important dyes by the preparation of composite hydrogels through an in situ incorporation of the chitosan into the network of several acrylic gels for the removal of the safranin T (ST) and brilliant cresyl blue (BCB) dyes from water.

2. Method

2.1 Materials

Monomers i.e. acrylic acid (AA, from Fluka), hydroxyethylmethacrylate (HEMA, from Fluka), N, N'-methylenebisacrylamide (MBA, from Fluka), Ammonium persulfate (APS, from Fluka) Sodium metabisulfite (SMBS, Merck). The natural polymer CS (>85% deacetylation) was procured from Fluka, USA and used as obtained. The Safranin T (ST) and Brilliant Cresyl Blue (BCB) dyes of analytical grade were purchased from SRL Chemical, India.

2.2 Hydrogels Synthesis

2.2.1. Poly (acrylic acid-co-hydroxyethyl methacrylate) gel.

Copolymer hydrogels were prepared by free radical crosslink copolymerization of acrylic acid and hydroxyl ethyl methacrylate in the presence of crosslinker MBA in water. The total amount of reaction volume was 50ml while the amount of total monomer in the reaction mixture (50 ml) was kept 25% (w/v). The molar ratio of acrylic acid and HEMA was fixed at 5:1. The polymerization reaction was carried out in a three necked glass reactor equipped with a mechanical stirrer, reflux condenser and thermometer. The dissolved oxygen of the reaction mixtures was removed by purging nitrogen gas for half an hour in the reaction mixtures before addition of the reacting monomers and crosslinker. After addition of the monomers and crosslinker the temperature of the reaction mixtures was raised to 60 °C with addition of the required amounts of redox pair of initiator, i.e., ammonium persulfate and sodium meta bisulfite. The reaction was then continued at this temperature till the reaction mixtures gelled. Several hydrogels were prepared by

varying initiator concentrations (0.5, 1.0, 1.5, and 2 wt.% of total monomer wt. with 1:1M ratio of persulfate and metabisulfite), crosslinker concentration (0.5, 1, 1.5 and 2 wt.% of total monomer wt.) and amount of chitosan (3, 6, 9 and 12 wt.% of total monomer wt.) in water.

2.2.2. Poly (sodium acrylate-co-hydroxyethyl methacrylate) gel.

The sodium salt of the copolymer gel was prepared in a similar way from sodium acrylate and hydroxyl ethyl methacrylate in the presence of MBA. The sodium acrylate monomer was prepared by drop wise addition of 1 M acrylic acid to 1 M sodium hydroxide solution in water kept on an ice bath till complete neutralization.

2.2.1.3. IPN gel of chitosan and copolymer.

For synthesizing the IPN gel, chitosan was first dissolved in water (1 wt.% chitosan and 2 wt.% acetic acid with respect to total solution volume) for half an hour followed by addition of comonomers to this viscous solution and stirring for another half an hour. Copolymerization of acrylic acid and hydroxyl ethyl methacrylate or sodium acrylate and hydroxyl ethyl methacrylate was allowed in the solution of chitosan in a similar way as in the case of the copolymer gel. The gel obtained was disintegrated in a blender, washed with water and then isopropyl alcohol, followed by filtration and finally dried to a constant weight at 30 °C in a vacuum oven.

By these solution polymerization methods four kinds of gels, namely poly (acrylic acid-co-hydroxy ethyl methacrylate), poly(sodium acrylate-co-hydroxyethyl methacrylate), IPN of chitosan and poly(acrylic acid-co-hydroxy ethyl methacrylate) and IPN of chitosan and (sodium acrylate-co-hydroxy ethyl methacrylate), designated as CP, SCP, CPCS and SCPCS, respectively were prepared.

3. Characterization of the Hydrogels

The synthesized hydrogels, i.e. CP, SCP, CPCS and SCPCS were characterized by FTIR, SEM, DTA-TGA, XRD.

3.1 FTIR

Fourier transform infrared (FTIR) spectra of the copolymer hydrogels were recorded on a FTIR spectrometer (Perkin Elmer, model-Spectrum-2, Singapore) using KBr pellet made by mixing KBr with fine powder of the polymer gel samples. (10:1 mass ratio of KBr to polymer). FTIR spectroscopy was studied to investigate structure of the hydrogels. The FTIR of CS, CP, SCP, CPCS and SCPCS gels are shown in Fig.1. For CS the absorption band at 3365 cm^{-1} corresponds to overlapping of -OH stretching and symmetric N-H vibration and also intermolecular hydrogen bonding of its polysaccharide moiety while C-H stretching vibration of CS is due to its 2912 and 2869 cm^{-1} band. The carbonyl stretching vibration (amide-I), N-H stretching vibration (amide-II) and the C-N stretching vibration (amide-III) of pure CS is indicated by its absorption at 1644, 1575 and 1313 cm^{-1} , respectively while peaks at 1373 and 1413 cm^{-1} are due to symmetrical deformation of its methyl (CH_3) groups [5]. CS shows another broad band appearing at 1079 cm^{-1} due to its C-O stretching. In Fig.3.3 the copolymer gel (CP) shows absorption peaks at 1639 and 3319 cm^{-1} for asymmetric stretching vibration of its carboxylic (COOH) and hydrogen bonded hydroxyl groups (O-H) present in its hydroxyethyl methyl acrylate moiety. Similarly, sodium salt of the copolymer, i.e., SCP shows an absorption peak at 1711 cm^{-1} corresponding to its acrylate (COO^-) [10] and also 3283 cm^{-1} due to hydrogen bonded hydroxyl groups. Some of these peaks disappear while most of these characteristic peaks are shifted in the composite gel viz. in CPCS and SCPCS as observed in Fig.1. Accordingly, the 3365, 2912, 1644, 1373 and 1079 cm^{-1} peaks of CS and 1639, 3319 cm^{-1} peaks of CP are shifted to 3298, 2921, 1676, 1399 and 1103 cm^{-1} in CPCS. Similar shifting and overlapping are also observed for SCPCS gel. All of these shifting and overlapping signifies strong electrostatic interaction such as hydrogen bonding between functional groups, intermolecular rearrangement and change in the configuration of the main chain of the two polymer moiety in the composite [11].

3.2. SEM

The surface morphology of the hydrogels were evaluated by SEM as shown in Fig.3.4 i), ii) and iii) for CS, CPCS and SCPCS, respectively. The SEMs were carried out at the same (1000x) magnification for comparison. It is observed that the copolymer CP shows a dense and featureless morphology while the presence of CS is evident in SEM of CPCS and SCPCS which shows two different phases viz, the CS is dispersed in the continuous copolymer phases. Pores and gaps are also observed in these two composite gels. In fact, introduction of CS facilitates pores and network structure in the composite as also reported elsewhere [12].

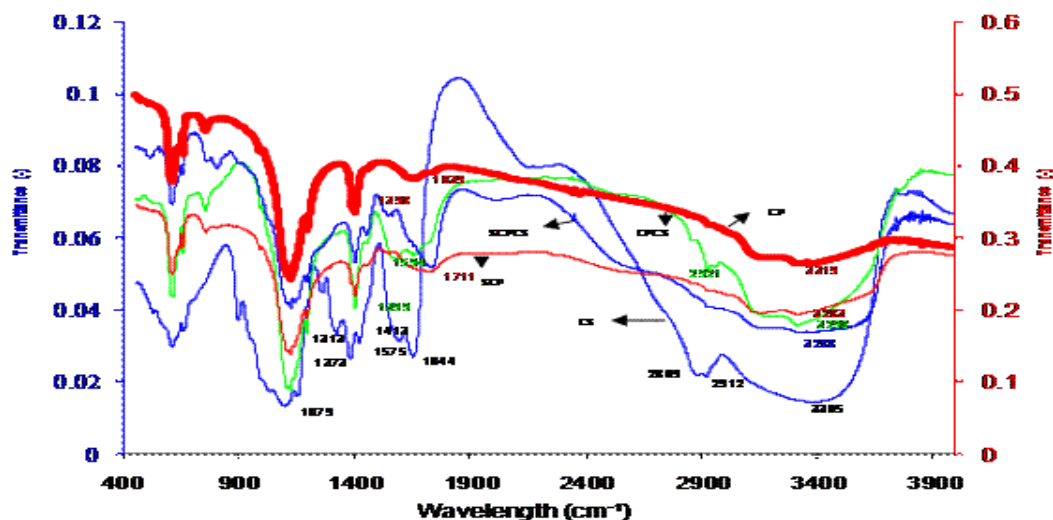
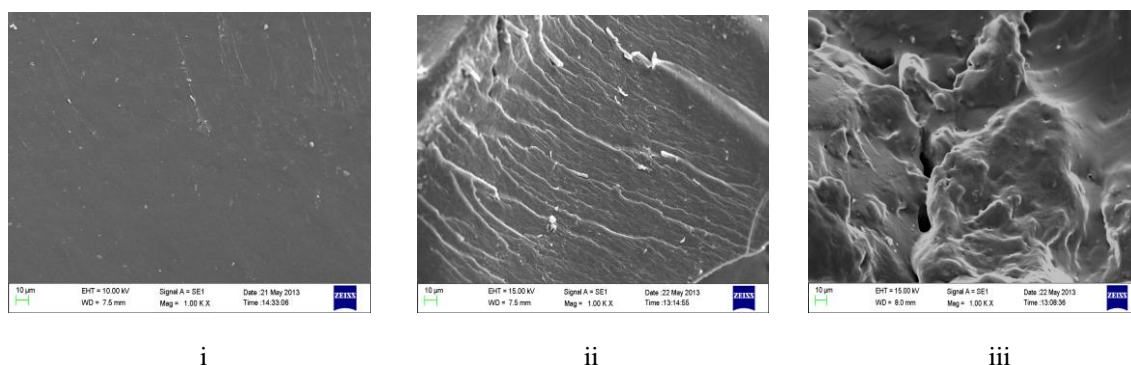


Fig.1. FTIR spectroscopy of the polymers



i

ii

iii

Fig. 2 SEM of the polymers, i) CP, ii) CPCS and iii) SCPCS

3.3 XRD

X-ray diffraction (XRD) characterizes the change of crystallinity of sodium alginate by IPN formation. Wide angle x-ray diffraction profile of the hydrogel samples were studied at 25°C with a diffractometer (model: X'Pert PRO, made by PANalytical B.V., The Netherlands) using Ni-filtered Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and a scanning rate of 0.005 deg(2 θ)/s). The angle of diffraction was varied from 2-72 degree. The XRD of the polymers are shown in Fig.3.6. The XRD of CS shows some crystallinity due to hydrogen bonding among its hydroxyl groups. Accordingly, CS is observed to show a strong diffraction peak at around 19.7° associated with mixture of (001) and (100) and one weak diffraction peaks at 10.06° associated with mixture of its (001) and (100) planes [5, 12]. However, in the composite gels, i.e., in CPCS and SCPCS the hydroxyl groups of CS forms chemical bond with copolymers (as also evident from FTIR analysis) and thus crystalline peaks of CS are not found in the composite gels.

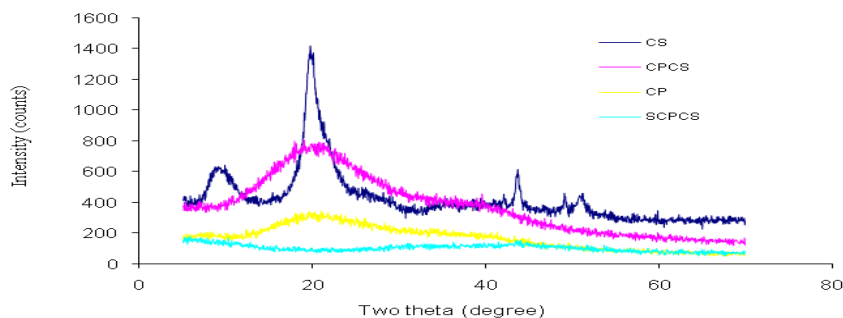


Fig.3.3. XRD of the polymers

3.4 DTA and TGA

Differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) of the hydrogel samples were carried out in a Perkin Elmer instrument in nitrogen atmosphere. The scanning rate was 10°C per minute in the temperature range of 60-600°C. The thermal properties viz. DTA and TGA of the hydrogel samples are shown in Fig.3.5. The decomposition of CS occurs in the temperature range of 255-340 °C with exothermic DTA peaks at 260 and 327 °C due to thermal decomposition of its amino and N-acetyl residue (Nam et al., 2010). The CPCS and SCPCS composite gels are observed to show endothermic peaks at 221 and 230° C, respectively due to formation of $-NH-CO-$ bond between protonated/non-protonated amine groups of CS and carboxylic/carboxylate groups of acid in the composite above 200 °C [13]. The TGA of the polymers are also shown in the same Fig.3.5. It is observed that CS shows two regions of weight loss viz., around 10% in the temperature range of 90-250°C due to loss of absorbed water and around 15-51% in the temperature region of 270-355 °C due to degradation of its main chain [14]. CS also shows a residue of about 27% at 580°C. The degradation of main chain of CS involves random splitting of its glycosidic bonds followed by further decomposition and formation of a series of lower fatty acids of C2, C3 and C6 [15]. From the same figure the copolymer CP is observed to show multiple degradation profiles viz. 5-10%, 15-35%, 40-70% and 75-80% degradation in the temperature range of 100-208 °C, 220-375 °C, 385-455 °C and 475-600 °C, respectively. However, the composite gels, i.e., CPCS and SCPCS shows two degradation profiles viz. CPCS shows around 10-40 % weight loss in the temperature region of 140-375 °C and 45-90% weight loss in the temperature range of 380-580°C while SCPCS shows 10-50% weight loss in the temperature region of 78-445 and 52-65% decomposition in the temperature region of 450-580°C. The first region (~5-10%) of degradation corresponds to loss of bound water while the degradations at other temperature regions may be ascribed to splitting of main chain and pendant hydroxyl and carboxylic groups of the polymer gels [15].

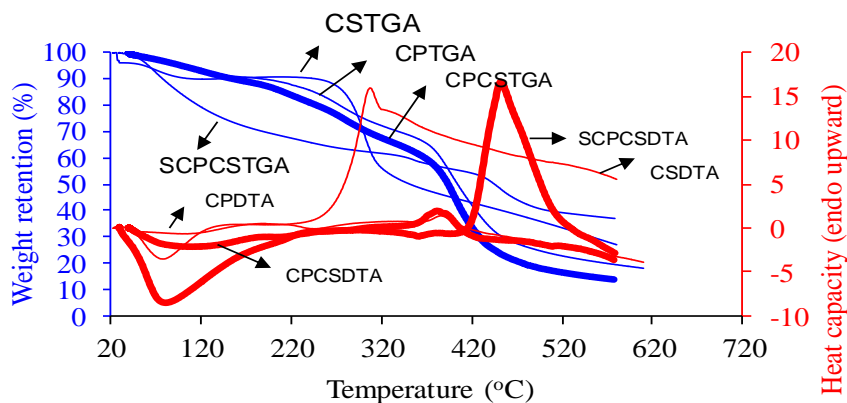


Fig. 3.5 DTA and TGA of the polymers

4. Results and Discussion

4.1. Study of swelling properties of the hydrogels

The variations of swelling ratio (SR) at different time intervals were obtained. The swelling was studied for hydrogels synthesized with different initiator, crosslinker and CS wt% and also at different solution pH. The swelling for composite hydrogels (CPCS) made with varied CS wt%. From these swelling properties it has been observed that initially SR increases with time and finally it levels off at an equilibrium value, i.e., equilibrium swelling ratio (ESR). There is no further increase in water uptake with time above this equilibrium value.

4.1.1. Effect of initiator and crosslinker (MBA) concentrations

The effect of varied initiator, crosslinker (MBA), CS concentration and solution pH on equilibrium swelling ratio (ESR) shows that with increase in initiator concentration from 0.5 wt% (of total monomer) to 2 wt%, ESR increases while ESR decreases due to increasing MBA concentration from 0.5 to 2 wt% (of total weight of acrylic acid and hydroxyethyl methacrylate monomer). The higher initiator concentration lowers molecular weight gel and thus more chain ends is formed. This leads to network imperfection and hence increased ESR [9]. Similarly, with increase in crosslinker concentration denser network is formed resulting in decrease in ESR [9]. Based on the ESR results, the initiator and crosslinker concentration were fixed at 1

wt% each for synthesis of gels with varied CS wt%. The gels obtained at these initiator and crosslinker concentration were mechanically stable with high ESR. The gels obtained at 0.5 wt% crosslinker showed the highest ESR but it was not mechanically durable. Similarly, gels obtained with initiator concentration higher than 1 wt% shows higher ESR but not stable because of low molecular weight.

4.1.2. Effect of CS

From the swelling it is observed that ESR increases with increase in wt% of CS in the gel. CS contains hydroxyl (-OH) and amine (-NH₂) polar functional groups in its structure. Thus, introduction of this functional polymer in the gel network increases ESR of the composite gel. However, CS also fills up the network of the gel. Hence above 12 wt% CS, ESR decreases (not shown). From the swelling results it is also observed that for the same CS % the composite gel of acrylate copolymer (SCPCS) shows much higher ESR than copolymer composite gel (CPCS). This may be ascribed to presence of excess negatively charged carboxylate functional groups (COO⁻ Na⁺) in SCPCS.

4.1.3. Effect of pH

From the above study it is evident that CPCS and SCPCS gel synthesized with 1 wt% initiator, 1 wt% crosslinker and 12 wt% CS showed the highest swelling characteristics. The swelling characteristics of these two composite gels at varied pH are also studied. It has been observed that with increase in solution pH, ESR of the hydrogel increases. This signifies the pH sensitivity of the hydrogels. The low ESR at acidic pH may be attributed to the hydrogen bonding interaction among the -COOH groups of the copolymer in the gel forming additional physical networks [16]. At low pH the small amount of CS present in the gel results in water uptake of the composite gels by electrostatic repulsion among its protonated amine (NH₃⁺) groups. At high pH the carboxylic groups are converted to carboxylate anions with expansion of the gel network due to electrostatic repulsion and therefore results in increased swelling.

5. Study of dye removal capacity of the hydrogels

The dye adsorption was studied by varying concentrations (10–140mg/L) of the two kinds of dye i.e. ST and BCB. These dye solutions were prepared in distilled water at different pH. 50 mg of hydrogel was taken in 100 cm³ of the dye solution [9] with continuous stirring on a magnetic stirrer until equilibrium was reached. The dye solution was separated by decantation from the hydrogel at equilibrium. The concentration of dye solutions before and after addition of hydrogel was determined by spectrophotometric measurement from a precalibrated curve of absorbance versus concentrations using Perkin Elmer lambda 2 5 UV-visible Spectrophotometer. The absorbance of the dye solution was measured at wavelength of 503 cm⁻¹ for ST and 624 cm⁻¹ for BCB dye. The amount of dye uptake (in mg) by unit mass (in g) of the hydrogel at equilibrium (Q_e , mg/g) and adsorption or removal% (R%) was calculated using the following equation-1 and 1a, respectively.

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1a)$$

Here C_0 and C_e are initial and equilibrium concentration of dye solution (mg/l) while V is volume (l) of the dye solution containing the hydrogel and m is mass (g) of the dry hydrogel polymer used for the experiment.

5.1. Effect of solution pH on dye adsorption

From the swelling results it is evident that the hydrogels are pH responsive. Hence, the influence of solution pH on dye adsorption was investigated. With change in solution pH, the ionization or polarization of various functional groups viz. -COOH, -OH, COOR, etc., present in the IPN hydrogels changes. Thus, the hydrogels are sensitive to change in pH of the solution. Accordingly, the dye adsorption properties of the hydrogels are also expected to change with solution pH. Thus, the effect of solution pH on adsorption of 100 mg/L of ST and BCB dye for the hydrogels were studied. Dye adsorption is observed from pH 4 to 7 for the two dyes. This may be ascribed to increase in ionization of carboxylate ions of the gels which increases abruptly above pK_a values of polyacrylic acid (~6.82) as reported elsewhere. Due to deprotonation of the amines groups of the dyes the adsorption decreases solution pH above 9.

5.2. Effect of contact time on dye adsorption

The effect of contact time of hydrogels on adsorption of ST and BCB was also studied. The dye adsorption properties are similar to that of swelling properties. Initially adsorption increases at a rapid rate followed by a slower rate of adsorption till it reaches equilibrium. At the beginning of the adsorption

experiment, the rate of adsorption is very high due to availability of the functional groups of the hydrogel for these interactions. As adsorption continues, there is exhaustion of the functional groups of the fixed amount of hydrogel present in the aqueous medium. Finally the rate of adsorption reaches a dynamic equilibrium with a maximum adsorption value. At this point the rate of adsorption by the hydrogel equals the rate of desorption from the hydrogel.

5.3 Effect of feed concentration on dye adsorption and dye removal%

The effect of the feed dye concentration on the adsorption and removal% of BCB and ST dyes for the three hydrogels at pH 7 had been studied. These hydrogels showed high adsorption and removal% for both BCB and ST dye. It is also observed that with an increase in the feed concentration, the dye adsorption increases while removal% decreases as the adsorption capacity of the hydrogel is fixed and at higher feed dye concentration the amount of dye left in the solution is also high [17]. For the feed concentration of 10–140mg/L of ST dye, the CP, SCP, CPCS and SCPCS gels show the adsorption of 8.9-68, 17-76, 23-85 and 33-93 mg/g gel, respectively with a removal% of 91-53%, 93-58%, 95-61% and 96-66% respectively. Similarly, adsorption of BCB dye for the same hydrogels show 9.3-71, 14-75, 26-87 and 28-95 mg/g gel, respectively with a removal% of 88-51.5%, 92-55%, 93-65% and 95.8-70%, respectively. These results are better than most of the reported results. For a feed dye concentration of 500mg/L, Kasgoz and Durmus [18] reported around 80% and 83% adsorption of ST and BCB dye, respectively with acrylamide-2-acrylamide-2-methyl propane sulfonic acid sodium salt (AMPSNa) hydrogel. Cole et al. [19] observed around 80% adsorption of ST dye for a feed dye concentration of 500mg/L with an organo clay incorporated copolymer of N-vinyl 2 pyrrolidone and itaconic acid. Akkaya et al. [20] reported 45% removal for ST and 90% removal for BCB dye with acrylic acid- acryl amidopropane hydrogel cross linked with 0.5wt% MBA for a feed dye concentration of 500mg/L dye. The high adsorption or removal% of the present hydrogels is caused by the strong electrostatic interaction among the functional groups of the cationic dyes with the anionic hydrogels. It has also been observed that for the same feed concentration, the present or reported hydrogels show higher adsorption and removal% for BCB dye than the ST dye. The ST dye shows less adsorption in comparison to BCB dye. This happens because ST contains four aromatic rings with one ring in other plane while BCB dye contains three fused aromatic rings. Hence, the ST dye shows more steric hindrance than BCB dye while coming in contact with gel adsorbent. Among the four gels, dye adsorption at any feed concentration is observed to increase in the following order CP>SCP>CPCS>SCPCS Although the sodium ion (Na⁺) competes to some extent with the cationic dye molecules in the adsorption process, the increased ionization and electrostatic repulsion of similar charges cause easier penetration of dye molecules in sodium poly acrylate based SCPCS hydrogel. For this reason it shows the highest adsorption. The copolymer based CPCS shows marginally lower adsorption than the SCP gel. In this case the bulky HEMA moiety may cause some steric hindrance to the approaching dye molecules.

6. Conclusion

Several hydrogels are synthesized from acrylic monomers, i.e., acrylic acid, sodium acrylate and hydroxyl ethyl methacrylate (HEMA) by *insitu* incorporation of varied amount of Chitosan during polymerization of these monomers. These hydrogels are characterized by FTIR, SEM, DTA-TG, XRD and swelling. These three IPN type gels are further used for adsorption study of two cationic dyes, i.e., ST and BCB. The two IPN gels show high adsorption and removal% for these two dyes.

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