Adsorption Efficiency versus Swelling Rates Of Chitosan Hydrogel Interpenetrating Network of Beads

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Abstract: *The presence of synthetic textile dyes in aqueous effluents, out streamed by industries causes terrible environmental pollution. Most of the synthetic textile dyes are recalcitrant, poisonous and degradation resistant, hence, naturally occurring polymers have been found to be an exceptional substance for biotechnological utilization due to having their distinct properties like biological compatibility with existing environment, non-toxicity and biodegradability. Chitosan, a deacetylated compound of chitin obtained from skin of crustacean fish is (1→ 4) 2- amino 2-deoxy β – D glucan and is now a familiar biodegradable polymer metabolized by human enzymes. It can be prepared as interpenetrating network of hydrogel as micro and nano sized beads, having a positive charge at wide pH range. These beads are attempted to remove some of metals and other pollutant from water. Chitosan beads of varying composition and crosslinked with glutaraldehyde have been prepared by us to study their removal efficiency for dyes and beads have been specified by using SEM and FTIR techniques. Experiments to study the swelling behavior of beads has been carried out to evaluate effect of bead composition (chitosan, crosslinker i.e. glutaraldehyde) and solution pH. The studies proved that swelling increased with increasing quantity of chitosan and with lowering the percentage of crosslinker. It is further concluded that the swelling percentage is more in acidic solution than in basic. Percent Color removal efficiency for dye from effluents has been determined and found to be dependent of dye initial concentration, pH, weight of chitosan, and also glutaraldehyde concentration. The results concluded that chitosan beads can be fruitful to remove color of effluents containing dyes and is able to improve water quality of effluents outflow from industries.*

Key words: *Dye, Effluent, FTIR, SEM, XRD, CRE*

I.   Introduction

The presence of synthetic textile dyes in aqueous effluents, out streamed by industries causes terrible environmental pollution. Most of the synthetic textile dyes are recalcitrant, poisonous and degradation resistant, hence, there is a necessity for the effective operation in real demand for manazing such industrial waste waters. During foregoing years, several methods have been explored and attempted to remove dyes from water effluents. Although some of these attempts were proved to be influenssive yet they have some or more limitations. Among these, adsorption is observed as a prominent process to decolorize waste water (1-6). The utilization of low-cost adsorbents is verified as a competent and profitable method to fade color of textile water. Studies have shown chitosan is proved to be such an adsorbent having good adsorption capacities. It is a deacetylated compound of chitin, (1→ 4) 2-amino-2 deoxy β – D glucan and well known biodegradable, non toxic polymer and metabolized by human enzymes. It is preferably used in a number of fields for examples food processing, pharmacology, biochemistry, textiles, agriculture, biotechnology and waste water treatment (7, 8). In search of low cost adsorbent, we tried to prepare chitosan beads crosslinked with glutaraldehyde having different composition which were then characterized and to explore their utility to decolorize industrial effluents.

II. Materials

Chitosan was supplied by India Sea Food, Kerala, and was used as received. Its percentage of deacetylation after drying was 89%. Glutaraldehyde and congo red dye were procured from Loba Chemie Pvt. Ltd, India.

III. Methods

Preparation of chitosan beads

Chitosan was dissolved in 2% acetic acid (40 ml) under stirring condition for three hours at room temperature. The homogeneous mixture was extruded as droplets using a syringe into NaOH -methanol solution (1:20 (w/w)) stirred continuously at 400 rpm. The produced beads were kept in a water jacket having glutaraldehyde in it and the temperature was maintained 50^oC for 10 minutes. Afterwards the beads were successively washed with hot and cold water and then vacuum dried.

Swelling Behaviour

Chitosan beads was carried out to swell up in different pH (2.0, 7.4 and 10.0) solutions. A weighed quantity (2.0 g) of the prepared beads was taken separately in the 50 ml conical flask containing solution. After predecided time period the swollen beads were separated and their net weight were determined after blotting the beads with filter paper to dry surface water on the beads. The swelling percentage at time t was calculated by the given formula-

Swelling percentage = $\{(W_t-W_o)/W_o\}$ x 100

Where, W_o and W_t are weights of the dried beads and weight after time t emersion in media.

Color removal efficiency (CRE)

10 ml dye solution of known concentration with 0.2 g of beads was taken in conical flask at desired temperature and pH. It was shaken for 10 min and then kept for 24 h and lastly the remaining concentration of dye was measured spectrophotometrically at λ_{max} of Congo Red (497 nm). The CRE (%) for CS beads was calculated by given formula -

CRE (%) = (1 – Ac/Ai) X 100

Where, Ai and Ac are the spectrophotometrically measured absorbance of the dye solution before and after the adsorption process.

Fourier transformed infra red (FTIR) spectroscopy

Dried samples were ground into powder and crushed with KBr for homogenization. The optically clear pellets were obtained using a Nicolet economy sample press whose were analysis and carried out using a Thermo Nicolet Avatar 370 FT-IR spectrometer system. Dry air as the chamber purge stream was utilized for whole range of samples. The FTIR spectra were produced at room temperature for a spectral frequency range of 400-4000 cm^{-1}. IR bands are expressed in terms of frequency (cm^{-1}). The background was prepared against a pure KBr pellet and the data analysis was carried out by omnic software. Functional groups present in the raw material and products were determined.

Scanning electron microscopy (SEM)

The bead surface and internal morphology with their shape and size were determined using FESEM QUANTA 200 FEG model "(FEI, The Netherlands make)" within the voltage range from 200 V to 30 kV. FESEM micrographs were obtained after beads surface coating with a very thin layer of gold by Sputter Coater (BAL-TEC AG, Balzers, Liechtenstein Company, Germany) model SCD-005 under atmosphere of argon to make the sample conducting. The surface appearance, shape and size of scanning electron micrograms were estimated to perform textural characterization of full and cross sectioned IPN beads. Magnifications were utilized to bead sample for estimating the exterior and interior of the bead.

IV. Results and Discussion

Chitosan hydrogel beads of different composition were prepared in laboratory as given in table (1).

Table–1 Composition of chitosan hydrogel beads

S.No.	Beads Code	Chitosan (g)	2% acetic acid (ml)	Glutaraldehyde (%)
1	B1	1.0	40	3.13
2	B2	1.0	40	6.25
3	B3	1.0	40	12.5
4	B4	0.8	40	12.5
5	B5	1.2	40	12.5

The beads are almost round in shape when freshly prepared but they become uneven in shape and also decreased their volume when dried. The colour of uncrosslinked beads was creamy which was changed into

yellow, later on, after crosslinking with glutaraldehyde. The yellow colour of crosslinked beads was turned into brown after air drying or oven drying.

Fourier Transform Infra Red Spectroscopy (FTIR)

FTIR curve in figure-1for chitosan exhibited a broad peak at 3450 cm^{-1} which was assigned to   –NH– stretching vibration which might be due to deacetylation of chitosan. The peak at around 3500 cm^{-1} due to hydrogen bonded O-H vibrational frequencies and O-H bond stretch of gluco pyranose units. Peaks at 1639 cm^{-1} and 1319 cm^{-1} were observed due to >C=O stretching of amide bond. The peak at 1613 cm^{-1} was assigned to strong N-H bending vibrations of secondary amide (8). Bands at 2919 cm^{-1}and 2810 cm^{-1} represent the aliphatic C-H stretching vibrations. The observed sharp peak at 1384 cm^{-1} is due to CH$_3$ symmetrical deformation mode (9, 10).Two peaks around 894 cm^{-1}and 1171 cm^{-1} appeared in spectra corresponding to saccharide structure (11). A broad band appearing near 1083 cm^{-1} indicated the >CO-CH$_3$ stretching vibration of chitosan.
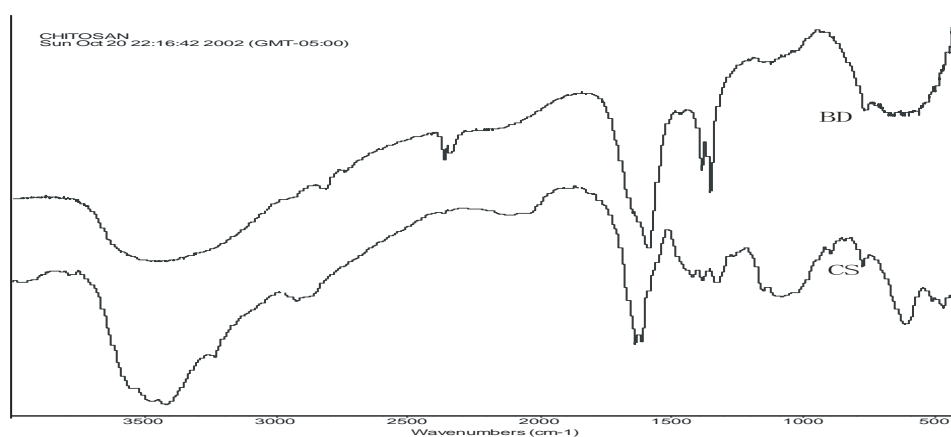

Figure 1-FTIR of pure chitosan powder (CS) and chitosan Beads (BD)

The structural changes in the beads were investigated using infra-red spectroscopy. It was concluded that during crosslinking, formation of the C=N group of the imine involved a reaction between the amino group of chitosan chain with aldehyde group of glutaraldehyde.

Scanning Electron Microscopy (SEM)

The surface appearance, shape and size of scanning electron micrograms were used to perform textural characterization of full and cross sectioned IPN beads. Magnifications were carried out for bead sample to estimate the outer and interior structure of the bead.
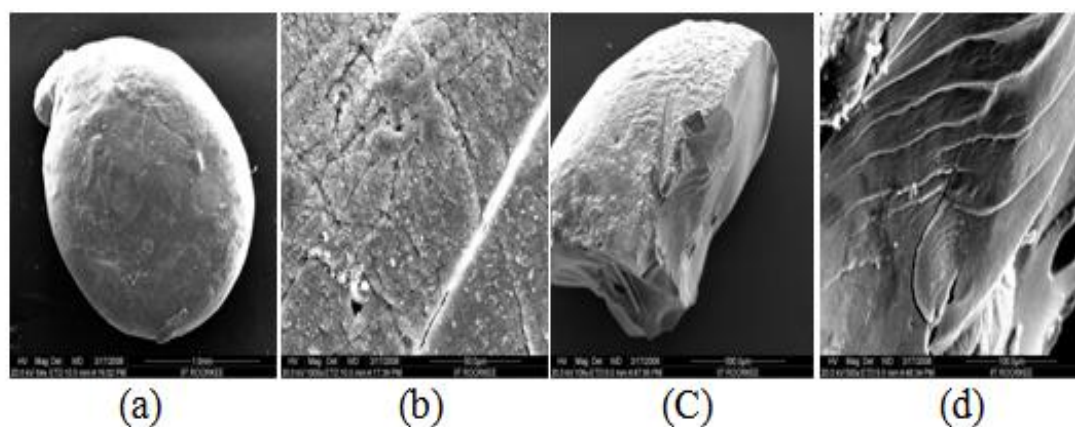

(a)　　　　　(b)　　　　　(C)　　　　　(d)

Figure 2– SEM micrographs of full chitosan bead (a), magnified bead (b), cross sectioned bead (c) and magnified cross sectioned bead (d)

SEM micrographs of full dried beads with their magnified (2000 X) surface morphology are shown in figure-2. It was concluded from the Figure 2a that the beads were nearly spherical or somewhat oval in shape. The approximate size of beads is 164 μm. They had rough, rubbery fibrous and folded surfaces with wrinkle (figure-2b).

The micrographs showing internal structure of beads with their magnification are obtained by half cut beads which are presented in Figure 2c and 2d. Interior of the beads appeared to have micropores and micro tube like interior spaces which confirms the highly porous structures of polymeric beads, although they appeared solid externally.

V. Swelling Studies

Effect of crosslinker

        The swelling percentage of crosslinked beads (B1–B3) varying in glutaraldehyde concentration were calculated as a function of time in pH 7.4 shown in figure-3. It was concluded that the rate of swelling for the crosslinked beads constituting different concentration of crosslinker glutaraldehyde follows the order B1 > B2 > B3 i. e. swelling rates increased with the decreased concentration of glutaraldehyde. When the cross linked beads are put into the solution, it penetrates into the beads and they subsequently try to swell. Generally, the long and coiled chains of polymer inside the crosslinked beads relaxed mechanically during the process of swelling. The crosslinking either chemical or physical in nature in between the polymeric chains provides a space between macromolecular network for diffusing the protons and other ions. The term 'degree of crosslinking' of a polymer is defined by the total molecular weight that exist between two consecutive crosslinks. Another major factor which also effective to measure the extent of swelling of hydrogel beads is the crosslinking density. It is the molar fraction of crosslinker to polymeric monomer units. If crosslinking density is higher that means greater number of crosslinker molecules are constituted to form polymeric networking within bead structure and thus have a mechanically stronger configuration of beads, hence, they will swell lesser as compare to beads forming lower value of crosslinking density or higher value of degree of crosslinking.
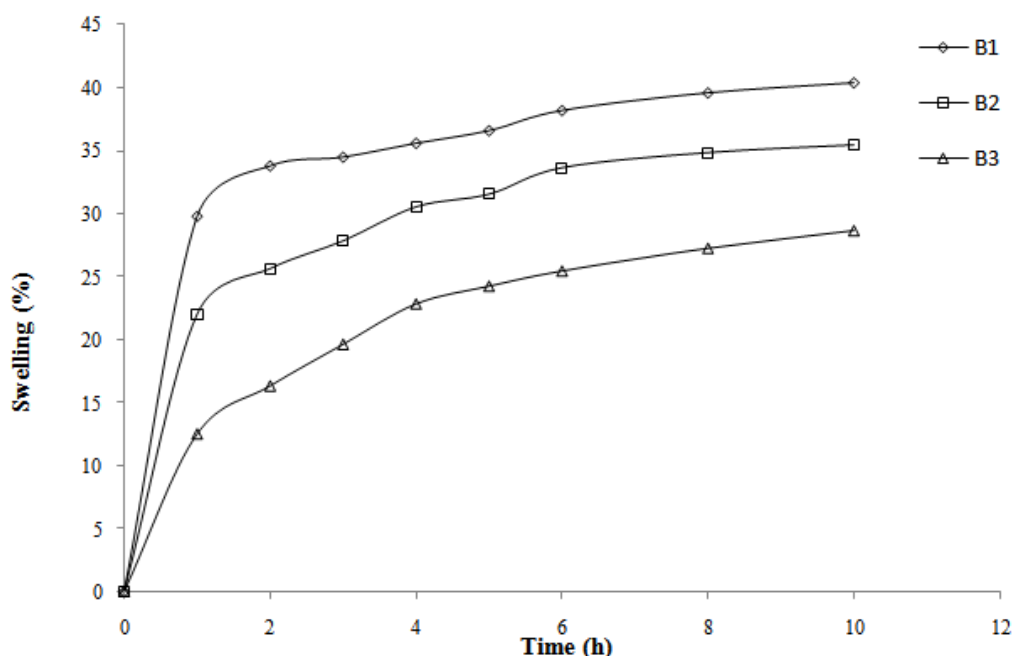
Figure–3 Plots of swelling rates showing the effect of glutaraldehyde concentration in CS beads at pH 7.4

        The flexibility of the polymer chain is hindered by crosslinking and the swelling rates became lower. The observation has been obtained from our studies that the degree of crosslinking accelerates the rate of swelling proportionally. Therefore, higher the crosslink density produced stronger beads with lower degree of swelling. It is the cause, due to having highest crosslink density or lowest degree of crosslinking B3 beads swell with lowest rate.

Effect of chitosan

        Experiments were carried out to study the effect of chitosan weight ratio on swelling percentage of crosslinked beads while incorporated same glutaraldehyde concentrations. The results are shown in figure–4. The swelling percentage of the crosslinked beads having 12.5% glutaraldehyde increases with enhanced concentration of chitosan in beads. The order is found such as B5 > B3 > B4.
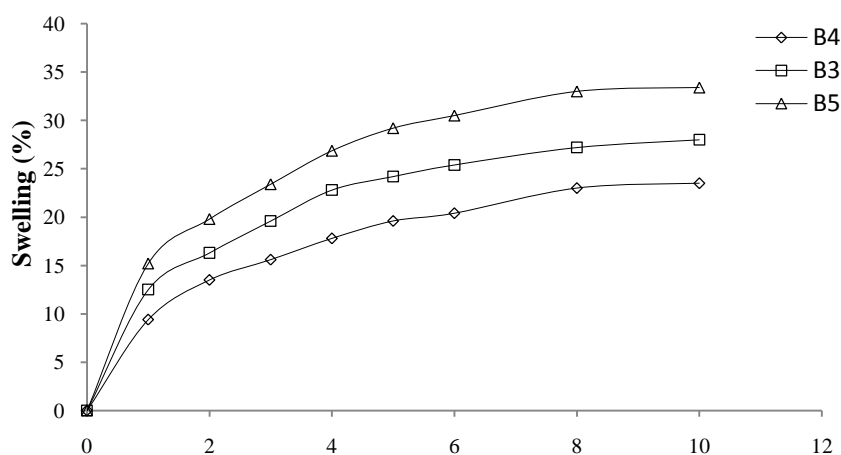
Figure– 4 Plots of swelling rates showing the effect of chitosan weight ration in CS beads at pH 7.4.

It can be explained as the weight of chitosan increased, the crosslinker density decreased and the diffusion of water into the beads become easier, which resulted in higher degree of swelling. The another reason is that the beads containing higher chitosan weight also had greater number of $-NH_2$ group to be protonated as $-NH_3^+$ i.e. an active adsorption site for dye anion.

The experimental studies to test the effect of concentration of glutaraldehyde or extent of crosslinking (figure 3) and weight of chitosan (figure 4) distinctly concluded that the beads B1 are swelled maximum, composed of 1.0 gm chitosan and 3.13 % of glutaraldehyde. As swelling provides increase sized pores allowing adsorbate ion to penetrate through it with more ease, hence B1 beads should have better adsorption efficiency. Keeping in view we have carried out our studies with B1 beads to explore its utility for adsorbing dyes from textile effluent.

Effect of pH

Swelling rates of B1 beads were studied in different solution having pH 2.0, 7.4 and 10.0 and the outcomes have been presented in figure–5 which was clearly indicated that swelling rates were highest in solution of acidic pH 2.0 and decreased on increasing the pH to 7.4 and the swelling is quite lowest in solution of alkaline pH 10.0. Actually, amino or imine groups of polymeric chain got protonated during the progress of swelling in acidic environment. Initially protonation of amino or imine groups easily found at the surface of beads occurred which prefer to dissociate hydrogen bonding of other functional groups to imino or amino group and make the polymeric coiled chain relaxed mechanically and provide spaces to diffuse protons and counter ions into the bead (12, 13).
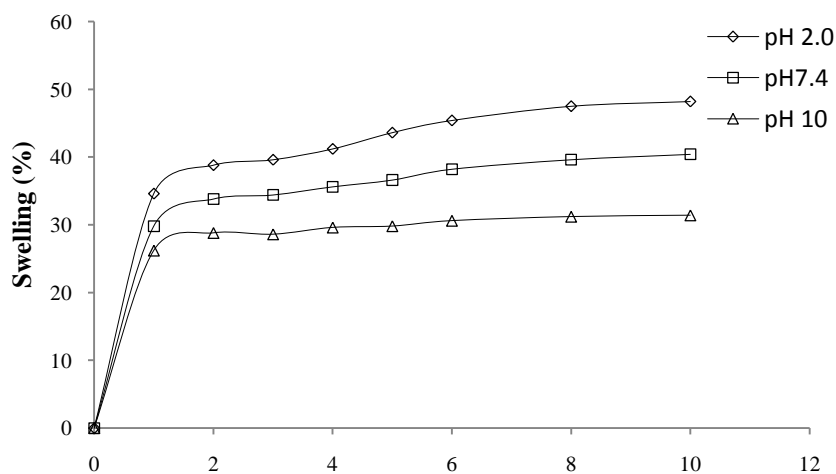

Figure-5 Swelling studies of chitosan beads at different pH

The swelling in alkaline medium (pH 10) was found to be lesser as compared to swelling in acidic solution (pH 2.0) due to inherent hydrophilicity of the chitosan beads dominating at acidic pH, therefore, encouraged slower swelling rates in neutral and alkaline media.

Color Removal Efficiency (CRE) of beads

Percent CRE is the measure of adsorption efficiency of CS beads. As the percent CRE increases at equilibrium after adsorption of dye on CS beads, the extent of adsorption increases. The factor affecting adsorption efficiency of CS beads as observed after experimentation are as follows-

Effect of pH

As absorbance measured for CR dye solutions are found to be stable at pH range 4.0–7.5. So we select pH 5.0 and 7.0 for adsorption experiment and results are presented in table–2

Table- 2 Percent CRE for CR dye at pH 5.0 and 7.0

S.No.	Bead type	% CRE at initial dye concentration			
		3.59×10^{-3} M		7.18×10^{-3} M	
		pH 5.0	pH7.0	pH 5.0	pH7.0
1	B1	28.63	21.56	73.56	61.38
2	B2	19.35	16.92	51.28	41.44
3	B3	13.65	12.59	43.87	39.66
4	B4	11.76	10.88	41.66	36.45
5	B5	13.89	12.83	44.22	40.17

% CRE or the extent of adsorption decreases with increasing pH of the dye solution. The % CRE is higher in acidic environment than in neutral (pH 7.0) medium as the swelling is higher in acidic pH and diffusion of dye anion is more easy through wider pores of swollen beads.

As the pH value increased from 5.0 to 7.0 the adsorption of dye onto chitosan beads from dye solution of same concentration of was decreased. Which can be explained on the basis of an electrostatic attractive forces exterted by the positively charged protonated amino groups($-NH_3^+$) inside the beads on the dyes anion and the chemical interaction between dye and chitosan beads (14). At acidic pH more of the protons were easily available to obtain increased number of active positive site on chitosan beads. This resulted increase in % CRE when the pH of the solution increased, the positive active sites on the surface decreased while negative charge sites increased on the beads while causes electrostatic repulsion and anionic dye not preferred to adsorb. Moreover, there was a competition between the hydroxide ions and dye anions that resulted a sharp lowering in adsorption. However, the anionic dye also get adsorbed significantly on chitosan beads still occur in alkaline media (15).

Effect of glutaraldehyde concentration

It can be explained that the extent of adsorption was increased on decreasing the concentration of glutaraldehyde and follow the order of B1 > B2 > B3, which is similar to the results that were obtained in the experiments of swelling studies. The increased concentration of glutaraldehyde increases the extent of crosslinking in the chitosan bead and decreases the pore size that caused restricted diffusion of pollutants through the polymer network and reduce polymer chain mobility. This is also due to decreased number of active site as a number of amino sites were engaged in crosslinking reaction (16) and the loss of active adsorption sites with the increasing concentration of crosslinker retarded the adsorption capacity of adsorbent.

Effect of chitosan weight

Adsorption capacity have been increased on increasing quantity of chitosan from 0.8 g to 1.2 g in beads for similar initial dye concentration and follows the order B5 > B3 > B4 in both acidic and neutral media.
This can be explained on the basis that the beads having lowest weight of chitosan (B4) must have lower number of free –NH$_2$ group which acts as adsorbing site for dye molecule in comparison to beads having highest weight of chitosan (B5).

Also beads having different CS weights were crosslinked with equal (3.13%) concentration of glutaraldehyde, hence B4 beads must have lower degree of crosslinking and so have smaller pore size and dye molecule must possess difficulty to diffuse through them to lower the rate of adsorption in comparison to B5. Again, similar order was obtained for rate of swelling in swelling studies experiment.

Effect of initial dye concentration

The % CRE of CR dye solutions for initial dye concentrations of 3.59×10^{-3} M and 7.18×10^{-3} M were given in table–2. It was found that on increasing initial dye concentration the %CRE was also increased sufficiently.

VI. Conclusion

The research observations clearly indicated that chitosan beads have good adsorbing capacity for CR dye. They show better colour removal efficiency which was depended of swelling percentage of beads. More of the swelling in beads produced enhanced dye removal efficiency. Results concluded that chitosan beads can be used as an adsorbent for CR dye removal from industrial effluent to remove its colour to make the water free of contamination.

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