



Poly(acrylamide) functionalized chitosan: An efficient adsorbent for azo dyes from aqueous solutions

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ABSTRACT

In the present communication we report on the optimization of persulfate/ascorbic acid initiated synthesis of chitosan-graft-poly(acrylamide) (Ch-g-PAM) and its application in the removal of azo dyes. The optimum yield of the copolymer was obtained using 16×10^{-2} M acrylamide, 3.0×10^{-2} M ascorbic acid, 2.4×10^{-3} M $K_2S_2O_8$ and 0.1 g chitosan in 25 mL of 5% aqueous formic acid at $45 \pm 0.2^\circ\text{C}$. Ch-g-PAM remained water insoluble even under highly acidic conditions and could efficiently remove Remazol violet and Procion yellow dyes from the aqueous solutions over a pH range of 3–8 in contrast to chitosan (Ch) which showed pH dependent adsorption. The adsorption data of the Ch-g-PAM and Ch for both the dyes were modeled by Langmuir and Freundlich isotherms where the data fitted better to Langmuir isotherms. To understand the adsorption behavior of Ch-g-PAM, adsorption of Remazol violet on to the copolymer was optimized and the kinetic and thermodynamic studies were carried out taking Ch as reference. Both Ch-g-PAM and Ch followed pseudo-second-order adsorption kinetics. The thermodynamic study revealed a positive heat of adsorption (ΔH°), a positive ΔS° and a negative ΔG° , indicating spontaneous and endothermic nature of the adsorption of RV dye on to the Ch-g-PAM. The Ch-g-PAM was found to be very efficient in removing color from real industrial wastewater as well, though the interfering ions present in the wastewater slightly hindered its adsorption capacity. The data from regeneration efficiencies for ten cycles evidenced the high reusability of the copolymer in the treatment of waste water laden with even high concentrations of dye.

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1. Introduction

The chemical contamination of water from a wide range of toxic derivatives, in particular heavy metals, aromatic molecules and dyes, is a serious environmental problem owing to their potential human toxicity. Therefore, there is a need to develop technologies that can remove toxic pollutants found in wastewaters. Dyes represent one of the problematic groups. Reactive dyes are the most common dyes used due to their advantages, such as bright colors, excellent color fastness and ease of application [1,2]. They exhibit a wide range of different chemical structures, primarily based on substituted aromatic and heterocyclic groups. A large number of reactive dyes are azo compounds that are linked by an azo bridge [3]. Many reactive dyes are toxic to some organisms and may cause direct destruction of creatures in water [4]. In addition, since reactive dyes are highly soluble in water, their removal from effluent is difficult by conventional physicochemical

and biological treatment methods [5,6]. Currently, a combination of biological treatment and adsorption on activated carbon is more common for the removal of dyes from wastewater [7]. Adsorption techniques are being widely used to remove certain classes of pollutants from waters, especially those that are not easily biodegradable. Adsorption has a specific advantage of removing the complete dye molecule, unlike certain removal techniques, which destroy only the dye chromophore leaving the harmful residual moieties in the effluent [8]. Although commercial activated carbon is a preferred sorbent for color removal, its widespread use is restricted due to high cost. For this reason, many researchers have investigated low-cost, locally available [9] biodegradable substitutes made from natural sources to remove dyes from wastewater [10–12]. It is well known that natural materials, waste materials from industry/agriculture and biosorbents can be obtained and employed as inexpensive sorbents. Developments in the synthesis of polysaccharide based adsorbents, in particular derived from chitin, chitosan, starch and cyclodextrin is of great importance. Chitosan [13,14] is a natural polymer obtained by alkaline deacetylation of chitin and finds applications as support material for gene delivery, cell culture and tissue engineering. Chitosan has the ability to adsorb substantial quantities of dyestuffs from aqueous solution.

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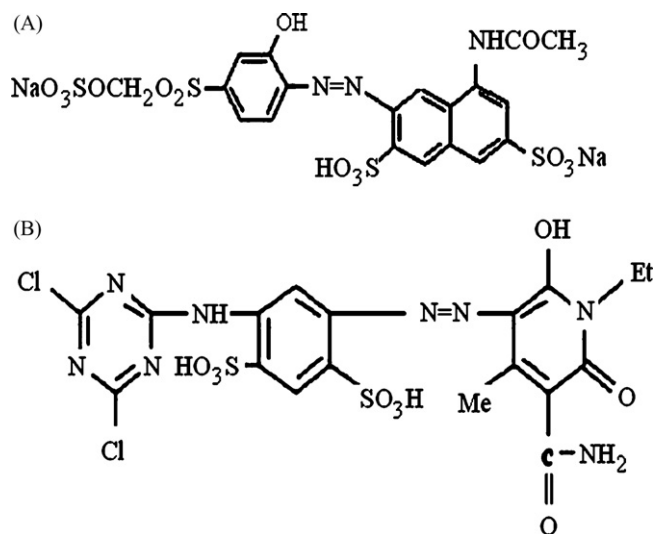


Fig. 1. Chemical Structure of dyes: A is Remazol brilliant violet; B is Procion yellow MX 8G.

Consequently, it may be a useful adsorbent for effluent treatment from textile mills. Physico-chemical investigation on the adsorption of Congo red [15] (an anionic azo dye) by chitosan hydrobeads has been carried out. Chitosan, dissolved in acetic acid, was used for the coagulation–floculation of an anionic dye “Reactive Black 5” [16] at low pH values. Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads has been studied [17] where removal increased with decreasing pH. Removal of dyes using chitosan has its drawbacks as its effectiveness as adsorbent is strongly pH dependent. Chitosan effectively removes dyes at acidic pH (pH 4), thus the pH of the wastewater has to be first adjusted on the acidic side, before treatment.

For a breakthrough in utilization, graft copolymerization onto chitosan will be a key point, which will introduce desired properties and enlarge the field of the potential applications of chitosan by choosing various types of graft chains. Earlier we reported [18] efficient removal of azo dyes using chitosan-graft-poly(methylmethacrylate) where efficient removal of the dyes were observed at pH 7. In the present communication, poly(acrylamide) grafting on to chitosan and application of the resulting copolymer in the removal of azo dyes from aqueous solutions has been undertaken. Batch adsorption experiments were carried out both for synthetic and industrial (effluent) samples. The effects of pH, initial concentration of the dye, adsorbent amount and contact time on the extent of dye removal are being reported. The reusability

of the prepared adsorbents for the treatment of wastewater over repeated cycles has also been evaluated.

2. Materials and methods

2.1. Reagents and stock solutions

High density chitosan flakes were acquired from ‘India Sea Foods’, Cochin, India and used without any further purification; the degree of deacetylation was 88%. Chitosan was ground to fine powders (>140 mesh) from flats and dried under vacuum at room temperature. Commercial chitosan was purified by dissolving in acetic acid and separating in alkaline solution and then extracting in a soxhlet apparatus by refluxing in alcohol for 24 h and drying at 60 °C in vacuum for 48 h before use. Acrylamide (Merck) in GR grade was used. Ascorbic acid and potassium persulfate (BDH, Analar Grade) were used without further purification. For Intrinsic viscosity determination, chitosan solution was made in 0.25 M CH₃COOH/0.25 M sodium acetate (Merck).

The two chosen dyes are structurally very different and are commercial dyes used without further purification. Stock solutions of Remazol brilliant violet (RV) and Procion yellow (PY) were prepared in water in 5 g/L concentration. The dyes were a gift from a dye manufacturing unit where its usage was high. Structural formula of dyes and characteristics of dyes are given in Fig. 1 and Table 1, respectively. UV–vis spectrum of Remazol brilliant Violet and Procion yellow dyes separately and their mixture is shown in Fig. 2. The industrial wastewater was procured from Threads India Limited, Kanpur, India. Characteristics of the wastewater are: Colour Pinkish yellow; pH 9.5; TDS 37,790 mg/L; TSS 3682 mg/L; COD 4480 mg/L; conductivity 1.237 mS; SO₄²⁻ 1045 mg/L.

2.2. Instrumental analysis

Copolymer sample of maximum %grafting was used for the characterization studies. Infra red (IR) spectra were recorded on a Bruker Vector-22 Infra red spectrophotometer using KBr pellets. X-ray diffraction (XRD) was carried out on Iodebexlex 2002 X-ray powder diffractometer. The pH of the solution was measured with a Digital pH meter (pHep Hanna instruments). The dye concentrations were measured at a wavelength corresponding to the maximum absorbance, λ_{max} by means of a UV–vis spectrophotometer (visible spectrophotometer (Systronics model 105). COD was measured using American Public Health Association (APHA) method [19]. The percentage of color removal was calculated by comparing the absorbance value of the supernatant to the standard curve obtained by a known dye concentration. Conductivity

Table 1
Details of the dyes.

	Color index (C.I.)	Type	λ _{max} (nm)	Absorbance (50 ppm)	pH
Remazol brilliant violet (violet)	Reactive violet 5R C.I. no 18097	Vinyl sulphone	560, 325	0.75, 0.62	7
Procion yellow MX 8G	Reactive yellow 86 C.I. 192755	Benzene disulfonic acid	416.94	0.65	7

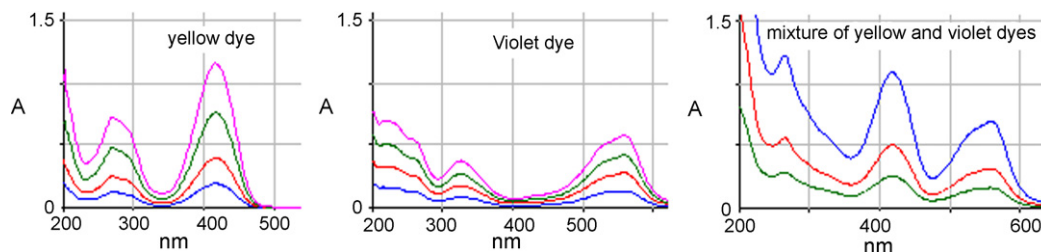


Fig. 2. UV–vis spectrum of yellow, violet and mixture of yellow and violet dyes at different concentrations.

was measured using micro processor conductivity meter. For intrinsic viscosity determination, flow time of the chitosan solution at five different concentrations was measured with Schott AVS 470 viscometer using 0.01 mm capillary. Viscosity average molecular weight of chitosan as calculated using Mark-Houwink-Sakurada equation [19] was 401.9 kDa.

2.3. Dye adsorption batch experiments

Adsorption experiments were carried out on a temperature controlled incubator shaker set at 120 rpm and maintained at 30 °C for 6 h. A known amount of adsorbent was thoroughly mixed with 20 mL of respective dye solution, whose concentration and pH was previously known. pH of the reaction mixture was initially adjusted to 2.0 using hydrochloric acid (1 M). No significant change in λ_{max} of dyes was observed with change in pH. After the flasks were shaken for the desired time, the suspensions were filtered through Whatman 0.45 mm filter paper and the filtrates after suitable dilutions, were analyzed for the dye concentration. Control experiments showed that no sorption occurred on either glassware or filtration systems.

The adsorption of RV by Ch-g-PAM was first optimized, keeping the other parameters constant, one parameter was varied at a time. For pH studies, 20 mL solutions of 600 ppm of dye solution was adjusted to various pH ranging from 2 to 10 and optimum pH was determined using 20 mg adsorbent dose. Various weights of the adsorbent ranging from 20 to 100 mg were used to study the effect of adsorbent dose on the adsorption of the dye at 2000 ppm concentrations. The effect of temperature on sorption of dyes was studied from 20 to 50 °C at 1000 ppm dye concentration using 20 mg adsorbent dose. The range for different initial concentrations dyes were 400–2000 ppm, using the 20 mg adsorbent dose. In order to evaluate kinetic data, the agitation time was varied from 30 to 360 min and the kinetic studies were done at 1000 ppm dye concentration and 20 mg adsorbent dose. Separate flasks were prepared for each time interval and only one flask was taken for desired time. Unless otherwise stated the experiments were carried out at dye concentration 1000 ppm, adsorbent dose 20 mg, working volume 20 mL, rpm 120 and shaking time 6 h. Calculation of amount of dye adsorbed by the adsorbent after spectrophotometer reading of equilibrium solution was obtained by calculating the difference using the formula:

$$q_e (\text{mg g}^{-1}) = C_0 - C_e (\text{mg L}^{-1}) \times \frac{V (\text{L})}{W (\text{g})} \quad (1)$$

where q_e is the amount of the dye adsorbed on the adsorbent, C_0 , the initial concentration of dye (mg/L), C_e , the equilibrium concentration of dye in solution (mg/L), V , the volume of the dye solution used (L), and W , the weight of the adsorbent used (g). To study the effect of structure of dye, the adsorption of yellow dye by prepared adsorbent was also carried out under the optimized conditions.

The industrial textile wastewater was mixed thoroughly (spiked) with a known amount of RV and PY dyes where a slight λ_{max} shift was observed for RV (567 nm, 328 nm). The adsorption of the dyes onto the adsorbents was studied using the American Dye Manufacturers Institute (ADMI) method [20] at pH 4. This method is applicable to colored waters and wastewaters having color characteristic. In the batch experiments, the spiked wastewater and 20 mg adsorbent were shaken in the shaker at 120 rpm and maintained at 30 °C for 6 h. Concentrated HCl was used to maintain the dye solution at pH of 4. At regular intervals, 0.1 mL of dye-mixture solution was taken out to dilute to a proper ADMI range (0–250 color unit (c.u.)). The ADMI color values were determined using the spectrophotometer with a narrow (10 nm or less) spectral band and an effective operating range of 200–700 nm

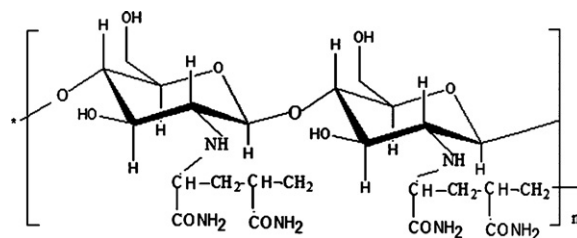


Fig. 3. Structure of Ch-g-PAM.

after the pH of diluted residual solution was adjusted to desired pH.

2.3.1. Desorption studies

In order to determine the reusability of the copolymer, after use it was stripped off with distilled water, 1N HCl, 1N H₂SO₄ and 1 M NaOH and reused, where the best results observed was for NaOH. To optimize the concentration of the alkali required for the quantitative stripping of the loaded dyes, experiments were carried out with varying concentrations of NaOH ranging from 0.01 to 1 M, where optimum stripping was possible with 0.1 M NaOH. Dye loaded copolymer samples were placed in the 0.1 M NaOH and stirred at 120 rpm for 2 h at 30 °C and the final RV dye concentration was determined. After each cycle the used copolymer was washed with distilled water and used in the succeeding cycle. The amount desorbed was calculated from the amount of dye loaded on the copolymers and the final dye concentration in the stripping medium. For the quantitative stripping, 2 h of equilibration time was required. Each sample after successive leaching was used thrice using 60 mg of the copolymer and 2000 ppm of RV dye solution in total volume of 20 mL.

2.4. Synthesis of chitosan-graft-poly(acrylamide)

Conditions for the adsorbent synthesis were optimized using the procedure described earlier [21]. Grafted chitosan (Fig. 3) was separated from polyacrylamide (PAM) by precipitating the reaction mixture with methanol:water (7:3). Finally, the grafted sample was extracted with methanol in a soxhlet apparatus for 4 h to dissolve all the homopolymer. The colorless product was dried under vacuum at 50 °C for 24 h to a constant weight (Ch-g-PAM). %G (%grafting) rafting and %E (%efficiency) were calculated [21] using the Eqs. (2)

Table 2

%Grafting and %efficiency at different monomer concentrations: [AA] = 2.1×10^{-2} ; [K₂S₂O₈] = 1.2×10^{-2} ; chitosan = 0.1 g, total volume 25 mL, 35 ± 0.2 °C.

S. no.	Monomer concentration (M)	%Grafting	%Efficiency
1	8×10^{-2}	26	18.28
2	10×10^{-2}	42	23.63
3	12×10^{-2}	55	25.89
4	14×10^{-2}	72	29.50
5	16×10^{-2}	95	33.41

Table 3

%Grafting and %efficiency at different [K₂S₂O₈] concentrations: [AA] = 2.1×10^{-2} ; [PAM] = 16×10^{-2} ; chitosan = 0.1 g, total volume 25 mL, 35 ± 0.2 °C.

S. no.	[K ₂ S ₂ O ₈] in M	%Grafting	%Efficiency
1	1.2×10^{-3}	95	33.41
2	1.5×10^{-3}	106	37.28
3	1.8×10^{-3}	115	40.44
4	2.1×10^{-3}	128	45.01
5	2.4×10^{-3}	135	47.48

Table 4

%Grafting and %efficiency at different [AA] concentrations: $[K_2S_2O_8] = 2.4 \times 10^{-3}$; $[PAM] = 16 \times 10^{-2}$; chitosan = 0.1 g, total volume 25 mL, $35 \pm 0.2^\circ C$.

S. no.	[Ascorbic acid] in M	%Grafting	%Efficiency
1	1.8×10^{-2}	105	36.93
2	2.1×10^{-2}	135	47.48
3	2.4×10^{-2}	147	51.70
4	2.7×10^{-2}	152	53.46
5	3.0×10^{-2}	165	58.03

Table 5

%Grafting and %efficiency at different temperatures: $[K_2S_2O_8] = 2.4 \times 10^{-3}$; $[PAM] = 16 \times 10^{-2}$; $[AA] = 3 \times 10^{-2}$, chitosan = 0.1 g, total volume 25 mL, $35 \pm 0.2^\circ C$.

S. no.	Temperature ($^\circ C$)	%Grafting	%Efficiency
1	35	165	58.03
2	40	172	60.49
3	45	280	63.20
4	50	175	61.55
5	55	152	53.46

and (3) and the results were summarized in Tables 2–6.

$$\text{Grafting ratio} = \frac{W_1 - W_0}{W_0} \times 100 \quad (2)$$

$$\text{Grafting efficiency} = \frac{W_1 - W_0}{W_2} \times 100 \quad (3)$$

3. Results and discussions

3.1. Characterization of the chitosan-graft-poly(acrylamide)

3.1.1. Fourier transform infra red spectroscopy

The IR spectra of the chitosan, Ch-g-PAM, RV dye and dye loaded chitosan, Ch-g-PAM and PAM-RV are shown in Fig. 4. IR spectrum of the RV dye is complex and shows many absorption peaks which includes phenolic O–H stretching at 3422 cm^{-1} , N–H stretching of secondary amide at 3340 cm^{-1} ; amide C=O stretching at 1658 cm^{-1} ; –S=O stretching of SO_3H group at 1398 cm^{-1} , O–H of – SO_3H group at 2919 , S=O stretching of – SO_3^- at 1176 cm^{-1} and N=N stretching at 1465 cm^{-1} .

PAM was water soluble and therefore it was not possible to obtain the dye loaded PAM. Spectrum of PAM and RV blend was taken for comparison. In the blend, N–H stretching peaks for primary amide groups are seen at 3340 and 3178 cm^{-1} , while amide I and amide II bands are seen at 1662 and 1608 cm^{-1} , respectively, while peaks due to N=N, sulphonic acid and sulfonate groups are seen between 1100 and 1500 cm^{-1} .

The IR spectrum of the chitosan showed strong peaks at 1030 , 1081 , and 1381 cm^{-1} , characteristic of saccharide structure (due to O–H bending, C–O stretching, and C–N stretching). The strong peak at 3434 cm^{-1} could be assigned to the stretching vibration of O–H, the extension vibration of N–H, and inter hydrogen bonds of the polysaccharide. The IR spectrum of synthesized Ch-g-PAM had additional peaks at 1664 (Amide I) and 1641 (Amide-II) due to grafted PAM chains at chitosan, while combined peak of O–H

Table 6

%Grafting and %efficiency at different chitosan wt.: $[K_2S_2O_8] = 2.4 \times 10^{-3}$; $[PAM] = 16 \times 10^{-2}$; $[AA] = 3 \times 10^{-2}$, total volume 25 mL, $35 \pm 0.2^\circ C$.

S. no.	Chitosan (mg)	%Grafting	%Efficiency
1	100	165	58.03
2	150	147	51.70
3	200	122	42.90
4	250	105	36.93
5	300	92	32.35

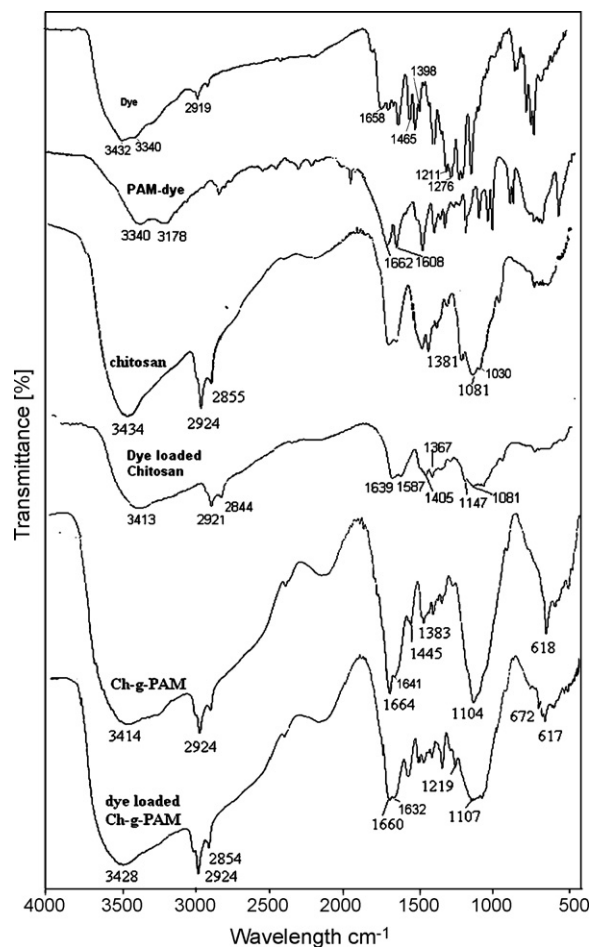


Fig. 4. FTIR of dye, PAM-dye, chitosan, dye loaded chitosan, chitosan-g-PAM and dye loaded Ch-g-PAM.

and N–H stretching in the grafted chitosan is seen at 3414 cm^{-1} . Significant changes in spectra of the RV dye loaded chitosan and Ch-g-PAM were observed after the adsorption. In dye loaded chitosan the combined O–H and N–H stretching peak has been shifted to 3413 cm^{-1} from 3434 cm^{-1} indicating significant contribution of N–H and O–H groups through complexation in the dye removal.

In Ch-g-PAM, stretching peak at 3414 cm^{-1} (O–H, N–H groups) shifted to longer wave number (3428 cm^{-1}) while amide I and amide II peaks are also seen shifted from 1664 to 1660 cm^{-1} and from 1641 to 1632 cm^{-1} and intensity of amide I peak has been reduced significantly after dye interaction. C–O stretching peak at 1104 cm^{-1} in the copolymer broadens in the dye loaded copolymer and the peak intensity has been reduced significantly. The sharp peak at 618 cm^{-1} due to C–N bending in the copolymer also broadens after the dye interaction. The IR spectra indicated that in adsorption of RV dye by Ch-g-PAM, amide carbonyls of PAM grafts have significant contribution.

3.1.2. X-ray diffraction

Comparison of the XRD pattern (Fig. 5) of chitosan with Ch-g-PAM further supports grafting. Chitosan has a sharp crystalline peak at $2\text{-theta } 21^\circ$, while the copolymer show reduction in the intensity of this peak, while new peaks at $2\text{-theta } 29\text{--}33^\circ$ and 45° appear due to the presence of PAM grafts at the polysaccharide molecule. In dye loaded copolymer, crystalline peaks are lost and the copolymer showed amorphous nature, indicating the loss of crystallinity on the binding.

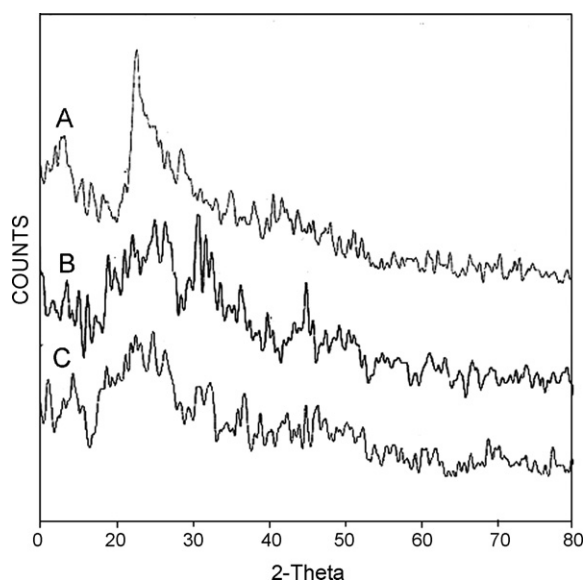


Fig. 5. XRD of (A) chitosan, (B) Ch-g-PAM and (C) Ch-g-PAM loaded with dye.

3.2. Effect of pH on the dye removal

The pH value of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. Similar observations have been reported by other workers for adsorption of reactive dyes indicating that the carbon skeleton of the dyes has a net positive charge on its surface [22]. The effect of pH on RV and PY dye removal both by Ch and Ch-g-PAM is shown in Fig. 6. It was observed that Ch-g-PAM was very efficient over a wide pH range of 2–8. The percentage removal of RV by Ch-g-PAM in pH range of 2–8 marginally varied from 92.7 to 97% at 600 ppm, being maximum at pH 4.0. On further increasing the pH to 10, the adsorption decreased to 78%. However for chitosan, adsorption was found pH dependent and was maximum at pH 4 (27%). PY followed a similar trend though the adsorption was slightly lower than that of RV dye both for chitosan and Ch-g-PAM. To compare the efficiency of Ch-g-PAM with the parent polysaccharide chitosan, all further studies were conducted at pH 4.

Chitosan (poly- β -(1 \rightarrow 4)-2-amino-2-deoxy-D-glucose) is an aminopolysaccharide, which is a cationic polymer produced by the N-deacetylation of chitin. It has high contents of amine and hydroxyl functional groups. At acidic pH, the anionic dye bearing sulfonic groups, is electrostatically attracted by protonated amine groups, thus neutralizing the anionic charges of dyes that can bind together. The removal of the dye reached a maximum with the complete neutralization of the anionic charges. With increasing

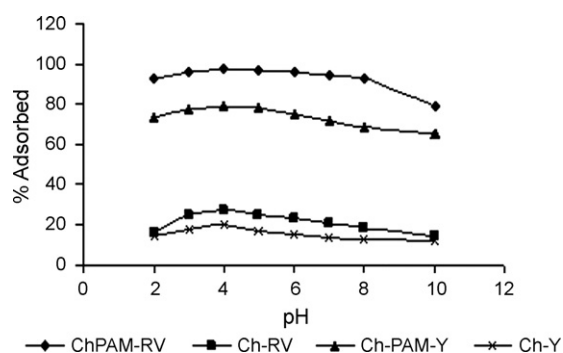


Fig. 6. Effect of pH on adsorption of RV and yellow dye by Ch and CH-g-PAM (20 mg in 20 mL for 600 ppm dye conc, 6 h stirring time).

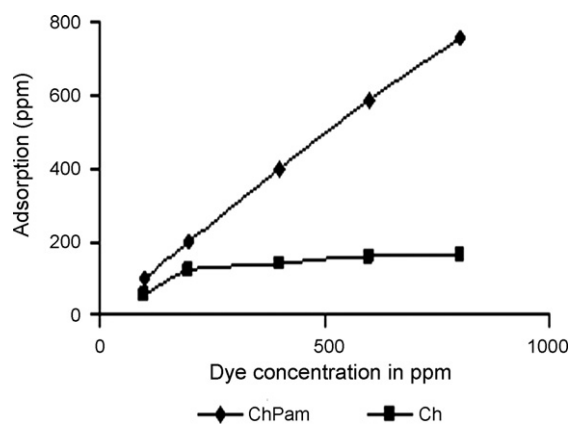


Fig. 7. Effect of initial concentration of RV dye on adsorption by Ch and Ch-g-PAM (adsorbent dose 20 mg).

pH, deprotonation of amino group takes place that results in poor interaction between the dye and the biopolymer and therefore the adsorption decreased. In the graft copolymer the adsorbent sites appear to be the grafted PAM chains (as supported by the IR spectra of the loaded copolymer) and therefore there is not much change in the adsorption efficiency of the grafted polymer over a wide range of pH. However at highly basic pH, alpha hydrogen from the amide groups in some of the grafted chains gets abstracted and due to electrostatic repulsion between the negatively charged grafts and the anionic dyes the adsorption is decreased slightly.

3.3. Effect of initial concentration of dye

The initial concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases. The experimental results demonstrating the effect of initial concentration of dyes on the removal by chitosan and Ch-g-PAM are shown in Fig. 7. Chitosan could adsorb 56 ppm of the dye at lower concentrations of 100 ppm which substantially increased to 162 ppm with increase in conc of dye to 600 ppm. Whereas the same amount of the polymer Ch-g-PAM could almost completely adsorb 400 ppm of dye initially. The increase of dye concentration in solution to 800 ppm increases adsorption up to 754 ppm. At high dye concentration, concentration of sorbate ions which could interact with the available binding sites at the adsorbent increase, hence higher uptake results.

3.4. Effect of adsorbent amount

In order to study the effect of adsorbent dosage on dye removal, various amounts of the adsorbent (20–100 mg) were contacted with a fixed initial dye concentration of 2000 ppm. It was observed on increasing the adsorbent dose, %removal of dyes increased. With Ch-g-PAM almost complete removal could be achieved at a dose of 60 mg or more whereas for chitosan only 37% removal could be achieved even with a high dose of 100 mg. With increase in the adsorbent dose, additional sorbent sites becomes available for adsorption and hence removal of dye molecules from the solution (Fig. 8). Also, with increasing adsorbent load, the quantity of dye adsorbed on to the unit weight of the adsorbent gets reduced, thus causing a decrease in q_e value with increasing adsorbent loading.

3.5. Effect of temperature

The effect of increasing temperature on the sorption was studied in the range of 20–50 °C for 1000 ppm RV and PY dyes using 20 mg adsorbent dose at pH 4.0. Though both the dyes followed a

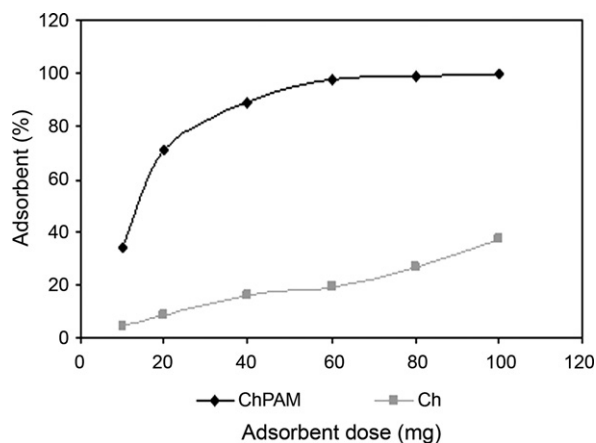


Fig. 8. Effect of adsorbent dose on adsorption of RV dye (2000 ppm dye).

similar trend, the adsorption of RV was more than that of PY. But at higher temperature PY adsorption increased significantly compared to RV with CH-g-PAM. The increase of adsorption of dyes with the increase in temperature (Fig. 9) is explainable since at higher temperature better interaction between the dyes and the adsorbent takes place due to increased collisions between them as the viscosity of the medium decreases. Adsorption of RV dyes increased from 88 to 94% with Ch-g-PAM whereas when chitosan was used, there was just a marginal increase from 17 to 19%, when the temperature was raised from 30 to 50 °C.

3.6. Adsorption equilibrium study

3.6.1. Sorption kinetics

%Removal of dye at a fixed adsorbent dose was monitored with time. The kinetics of dye removal by Ch-g-PAM indicated rapid binding of dye to the sorbent during the first few minutes, followed by a slow increase until a state of equilibrium at 6 h was reached. No

change in the uptake capacity was observed with further increase in equilibration time up to 24 h. The initial rapid phase may be due to increased number of vacant sites available at the initial stage, as a result there existed an increased concentration gradient between adsorbate in solution and adsorbate in the adsorbent [23]. Generally, when adsorption involves a surface reaction process, the initial adsorption is rapid. Then, a slower adsorption would follow as the available adsorption site gradually decreases. Kinetics of sorption was modeled by the first order Lagergren equation, the pseudo-second-order equation and the second-order rate equation shown below as Eqs. (4)–(6), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{K_L t}{2.303} \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k' q_e^2} + \frac{t}{q_e} \quad (5)$$

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (6)$$

where K_L is the Lagergren rate constant of adsorption (min^{-1}); k' the pseudo-second-order rate constant of adsorption (g/mg/min) and k_2 the second-order rate constant (g/mg/min); q_e and q_t are the amounts of dye sorbed (mg/g) at equilibrium and at time t , respectively. The kinetics of RV dye adsorption by Ch-g-PAM was modeled by Lagergren equation, the pseudo-second-order equation and the second-order rate equation (Fig. 10). It was observed that the adsorption kinetic data of the dye adsorption on Ch-g-PAM are well represented by pseudo-second-order model where linear plot of t vs t/q_t was obtained with the correlation coefficient (R^2) being 0.9924, for RV dye where the rate constants were calculated to be 2.59×10^{-5} g/mg/min .

3.6.2. Adsorption isotherms

Adsorption data were fitted to the Langmuir and Freundlich isotherms. The Langmuir isotherm is valid for monolayer sorption due to a surface of a finite number of identical sites and expressed

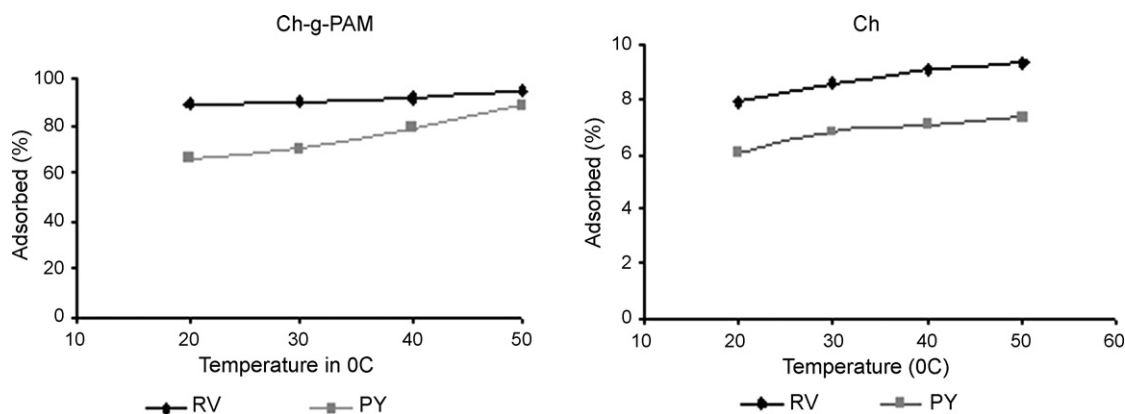


Fig. 9. Effect of temperature on adsorption of RV and PY dye both by Ch and Ch-g-PAM.

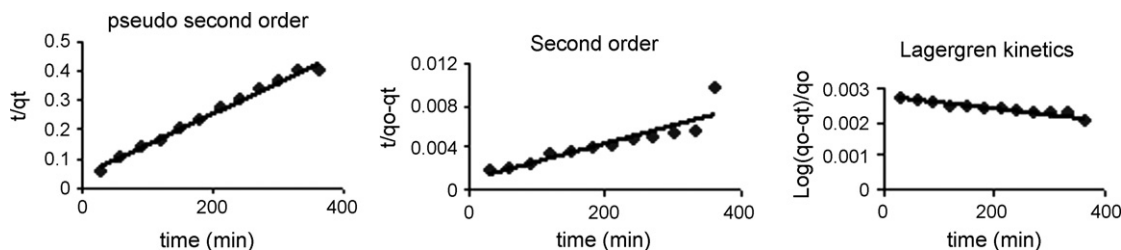


Fig. 10. Pseudo-second-order, second-order and Lagergren kinetics with CH-g-PAM as adsorbent for RV dye.

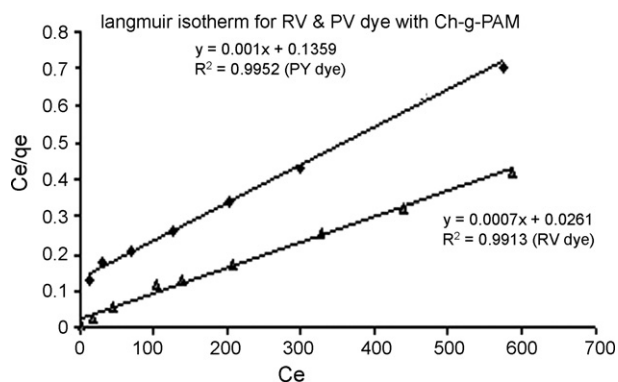


Fig. 11. Langmuir isotherm with CH-g-PAM as adsorbent for RV and PY (yellow) dye.

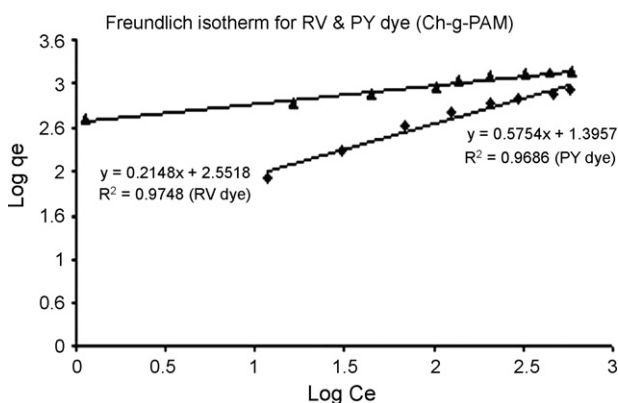


Fig. 12. Freundlich with CH-g-PAM as adsorbent for RV and PY (yellow) dye.

in the linear form as under

$$\frac{C_e}{q_e} = \frac{b}{Q_0} + \frac{C_e}{Q_0} \quad (7)$$

where C_e is the equilibrium concentration (mg/L) and q_e the amount adsorbed at equilibrium (mg/g). The Langmuir constants Q_0 (mg/g) represent the monolayer adsorption capacity and b (L/mg) relates the heat of adsorption. The essential feature of the Langmuir adsorption can be expressed by means of R_L , a dimensionless constant referred to as separation factor or equilibrium parameter for predicting whether an adsorption system is favorable or unfavorable. R_L is calculated using the following equation

$$R_L = \frac{1}{1 + bC_0} \quad (8)$$

where C_0 is the initial dye concentration (mg/L). If R_L values lies between 0 and 1, the adsorption is favorable.

The Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (9)$$

where K_f indicates adsorption capacity (mg/g) and n an empirical parameter related to the intensity of adsorption, which varies with

Table 8

Thermodynamic parameters for the adsorption of RV on Ch-g-PAM.

Dye	Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
RV	293	-19.138	+17.8	+0.0773
	303	-19.136		
	313	-19.138		
	323	-19.138		

the heterogeneity of the adsorbent. The greater the value of the n , favorable is the adsorption.

Adsorption of RV and PY dyes at pH 4, by Ch-g-PAM was modeled by Langmuir (Fig. 11) and Freundlich adsorption (Fig. 12) equations (Table 7). The data fitted better to Freundlich isotherm indicating surface homogeneity of the adsorbent and unilayer adsorption.

In adsorption by Ch-g-PAM at pH 4, Q_m was found to be 1428.57 with monolayer adsorption capacity 'b' 0.02681 (1/mg) for RV dye in comparison with chitosan itself [18] where Q_m and 'b' were 122 and 0.1677 for the RV dye at same pH.

3.6.3. Adsorption thermodynamics

The thermodynamic parameters including change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), were determined by using Van't Hoff equation.

$$\log \frac{C_{ac}}{C_{eq}} = -\frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R} \quad (10)$$

where C_{ac} is the amount adsorbed on solid at equilibrium and C_{eq} is the equilibrium concentration. The change in free energy is calculated using equation

$$\Delta G^H = -2.303RT \log \frac{C_{ac}}{C_{eq}} \quad (11)$$

The values for RV dye adsorbed by Ch-g-PAM are listed in Table 8.

The negative value of ΔG° indicates the spontaneous nature of adsorption process. The positive ΔH° indicates the endothermic nature of dye adsorption onto Ch-g-PAM indicating some chemical binding between the dye and the adsorbent material. The positive values of entropy change indicate randomness at the solid/solution interface. As $\Delta H^\circ > 0$ i.e. higher temperature will facilitate the adsorption of dye onto Ch-g-PAM. The positive value of ΔS reveals the increased randomness at the solid–solution interface during the fixation of the dye molecule on the active site of the adsorbent. Since the adsorption process is endothermic; it follows that under these conditions the process becomes spontaneous because of the positive entropy change.

3.7. Removal of color from real wastewater

The wastewater from industry usually contains more than one dye and many ions in a combination. To study the adsorption behavior of the dyes, they were spiked in real textile wastewater as a binary mixture. Adsorption of the dye onto chitosan and Ch-g-PAM (both at pH 4) were studied by the removal of ADMI from the aqueous solutions. ADMI removal percent (%) is the ratio between the removal ADMI value at any contact time and the ADMI value at initial concentration (Fig. 2B). The %removal in real industrial waste increases with increase in the adsorbent dose.

Table 7

Langmuir and Freundlich isotherm constants for CH-g-PAM.

Dye	Langmuir isotherm			Freundlich isotherm		
	Q (mg/g)	b (L/mg)	R^2	n	K_f (mg/g)	R^2
RV	1428.57	0.02681	0.9913	4.6554	741.78	0.9748
PY	1000.00	0.00736	0.9952	1.7379	24.877	0.9686

Table 9
Adsorption from wastewater additionally spiked with RV dye (1000 ppm).

Adsorbent dose (mg)	CH-g-PAM	CH
20	540	70
40	855	232
100	988	688

Using 40 mg adsorbent dose and 1000 ppm dye concentration, chitosan remove 23.24% textile waste color where as CH-g-PAM shows 85.55% adsorption under identical condition (Table 9). But almost complete removal could be achieved when the Ch-g-PAM dose was increased to 100 mg unlike chitosan which could attain a maximum of 68% removal under identical conditions.

In the combination study (using 20 mg adsorbent dose, pH 4.0, 120 rpm at 30 °C) where binary dye mixtures (RV and PY 600 ppm each) were used the adsorption decreased significantly, and 86.15 for RV and 62.7% for PY. This decrease is attributed to the interference of dyes in the adsorption process. When 1000 ppm of each dye was spiked in the industrial waste water using 20 mg of the adsorbent at pH 4.0 the adsorption of the RV and PY dye decreased to 20 and 15% from 77 and 57%, respectively (Fig. 13). On increasing the adsorbent dose from 20 to 100 mg 79.3% of PY and 87.5% RV could be removed easily. While chitosan (100 mg) at the same time could remove only 19.6% PY and 37.6% RV from the dye spiked waste water under identical conditions. The decreased adsorption of the dyes spiked in waste water is due to the other interfering ions and dyes materials present in the waste water.

3.8. Desorption studies.

The prepared copolymer Ch-g-PAM was tested for its adsorption capacity in terms of its reusability for consecutive 10 cycles. 60 mg of the adsorbent could almost completely adsorb 2000 ppm of RV dye. Almost complete (96.7%) desorption of the loaded dye in 2 h could be achieved using 0.1 M NaOH in the 1st cycle. The copolymer in the next five consecutive cycles showed similar performance with almost 94% adsorption and a loss of 1–2% dye during stripping. The used graft copolymer even in the 7th cycle could adsorb 81.5% dye, which could be desorbed up to 71.4%. Thereafter the adsorbent showed a steady decline in its performance, both in adsorption as well as desorption. In the last 10th cycle only 29.04% adsorption and 20.69% desorption was observed (Fig. 14). Though the %removal decreased per cycle, the pronounced decrease was observed only after the 5th cycle, suggesting that the uninhibited efficiency of the copolymer for a very long time and that too for very high concentration of the dye. Hence, it appeared that during des-

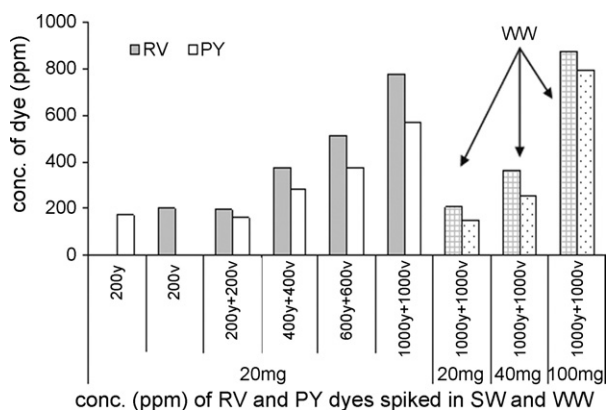


Fig. 13. Ch-g-PAM (20 mg) as adsorbent for synthetic water (SW) and real wastewater (WW) spiked with different concentrations of binary mixture of RV (v) and PY (y) dyes. The WW shows increasing dose of adsorbent.

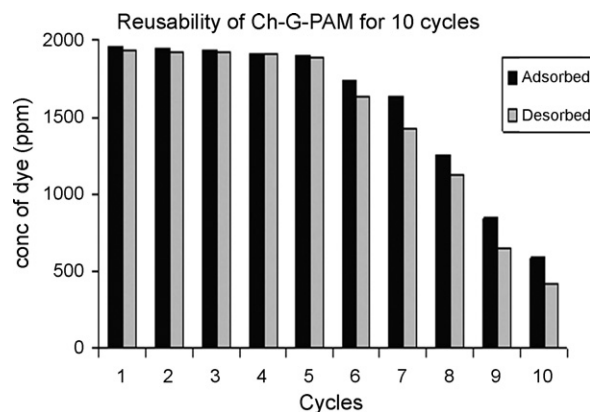


Fig. 14. Reusability of Ch-g-PAM by adsorption–desorption process for 10 consecutive cycles.

orption only the textile dyes, which were electrostatically adsorbed were desorbed. It was likely that both electrostatic and complexation reaction occurred between the sorbent and the metal ion; therefore complete desorption was not possible moreso in the later cycles.

4. Conclusions

Ch-g-PAM proved to be a very effective adsorbent as compared to parent chitosan for the removal of anionic dyes from synthetic dye solution as well as real textile wastewater. The adsorption is dependent on concentration and temperature of the solution, while pH has little effect on the adsorption of dyes by Ch-g-PAM (in the pH range of 2–8). Equilibrium adsorption of dyes in synthetic solution was achieved in about 6 h. Adsorption kinetic followed pseudo-second-order kinetic model confirming the chemisorption of dyes onto grafted copolymer. The grafted CH-g-PAM could be an excellent adsorbent for the removal and recovery of dyes from industrial textile effluent as exhibited by its reusability potential for almost 10 cycles.

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