

Poly(methylmethacrylate) grafted chitosan: An efficient adsorbent for anionic azo dyes

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ABSTRACT

Present study reports on peroxydisulfate/ascorbic acid initiated synthesis of Chitosan-graft-poly(methylmethacrylate) (Ch-g-PMMA) and its characterization by FTIR, XRD and ¹³C NMR. The copolymer remained water insoluble even under highly acidic conditions and was evaluated to be an efficient adsorbent for the three anionic azo dyes (Procion Yellow MX, Remazol Brilliant Violet and Reactive Blue H5G) over a wide pH range of 4–10 being most at pH 7. The adsorbent was also found efficient in decolorizing the textile industry wastewater and was much more efficient than the parent chitosan. Equilibrium sorption experiments were carried out at different pH and initial dye concentration values. The experimental equilibrium data for each adsorbent-dye system were successfully fitted to the Langmuir and Freundlich sorption isotherms. Based on Langmuir model Q_{\max} for yellow, violet and blue dyes was 250, 357 and 178, respectively. Thermodynamic parameters of the adsorption processes such as ΔG° , ΔH° , and ΔS° were calculated. The negative values of free energy reflected the spontaneous nature of adsorption. The adsorption kinetic data of all the three dyes could be well represented by pseudo-second-order model with the correlation coefficients (R^2) being 0.9922, 0.9997 and 0.9862, for direct yellow, reactive violet and blue dye, respectively with rate constants 0.91×10^{-4} , 1.82×10^{-4} and $1.05 \times 10^{-4} \text{ g mg}^{-1} \text{ min}^{-1}$, respectively. At pH 7, parent chitosan also showed pseudo-second-order kinetics. The temperature dependence of dye uptake and the pseudo-second-order kinetics of the adsorption indicated that chemisorption is the rate-limiting step that controls the process.

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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 the 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 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 physico-chemical and biological treatment methods [5,6]. These days, 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 [7,9,10–13]. Many natural as well as industrial and agricultural waste materials are employed as inexpensive biosorbents. Developments in the synthesis of polysaccharides based adsorbents, in particular modified biopolymers derived from chitin, chitosan, starch and cyclodextrin [14] are of great importance. Chitosan [15,16] 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

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has the ability to adsorb substantial quantities of dyestuffs from aqueous solutions. Consequently, it may be a useful adsorbent for effluent treatment from textile mills. Physico-chemical investigation on adsorption of Congo red [17], an anionic azo dye by chitosan hydrobeads has been carried out. Chitosan, dissolved in acetic acid, was used for the coagulation–flocculation of Reactive Black 5, an anionic dye [18] at low pH values. Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads has been studied [19], where removal increased with decreasing pH. Effectiveness of chitosan in the dye removal is strongly pH dependent. For a breakthrough in its utilization, vinyl grafting onto chitosan will be a key point, which can introduce desired properties and enlarge the field of its potential applications by choosing various types of side chains. Graft copolymers might prove potentially better candidates for dye removal from the wastewater than the parent polysaccharides due to the presence of grafted chains [20]. The present work describes the synthesis and application of the poly(methylmethacrylate) grafted chitosan for the removal of structurally different azo dyes. Batch adsorption experiments were carried out both for synthetic and industrial (effluent) samples. The effects of %G, pH, initial concentration of the dye, adsorbent amount, temperature and contact time on the extent of dye removal are being reported.

2. Experimental

2.1. Materials

Chitosan flakes (low molecular weight; degree of deacetylation, 88%) were acquired from 'India Sea Foods', Cochin, India and used without any further purification after grinding to fine powders (>140 mesh) from flats and drying under vacuum at room temperature. Methylmethacrylate (Merck) was washed with 5% aqueous alkali to remove phenolic inhibitor and then vacuum distilled before use. Ascorbic acid and potassium persulfate (BDH, Analar Grade) were used without further purification.

Dye stock solutions (5 g in 1 L of distilled water) of Procion Yellow MX (yellow), Remazol Brilliant Violet (violet) and Reactive Blue H5G (blue) were prepared. The dyes were a gift from a dye manufacturing unit (where the usage of these dyes was high) and were used as it is without further purification. The details of the dyes are given in Table 1, Fig. 1. The industrial wastewater was procured from Threads India Limited, Kanpur, India. Characteristics of the wastewater are: pinkish yellow color, 9.5 pH, 37790 mg L⁻¹ TDS, 3682 mg L⁻¹ TSS, 4480 mg L⁻¹ COD, 1045 mg L⁻¹ SO₄²⁻ and 1.237 ms conductivity. The visible spectrum of the dyes and the spiked wastewater is shown in Fig. 2.

2.2. Synthesis of Chitosan-graft-poly(methylmethacrylate) (Ch-g-PMMA)

Conditions for the adsorbent synthesis were optimized using the following procedure. To a calculated amount of chitosan solution (25 cm³ of 5% aqueous formic acid), calculated amount of methylmethacrylate and ascorbic acid were added and the reaction

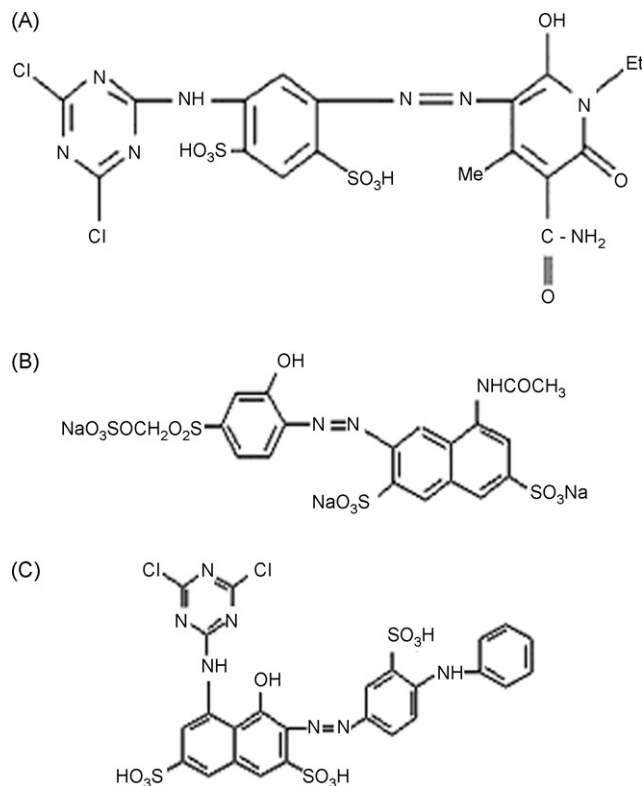


Fig. 1. Chemical structures of the dyes: (A) Procion Yellow MX 8G; (B) Remazol Brilliant Violet 5R; (C) Reactive Blue 81.

mixture was thermostated on water bath at known temperature. After 30 min, calculated amount of K₂S₂O₈ was added and this time of addition of persulfate was taken as zero time. Graft co-polymerization was allowed for 1 h. Ch-g-PMMA (Fig. 3) was separated [20,21] from poly(methylmethacrylate) (PMMA) by precipitating the reaction mixture with acetone where upon the PMMA dissolves and copolymer is precipitated that was filtered and dried. Finally, the grafted sample was extracted with acetone 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-PMMA). %G and %E obtained in different sets of experiments were calculated using following equations and the results have been summarized in Tables 2–5.

$$\%Grafting(\%G) = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

$$\%Efficiency = \frac{W_1 - W_0}{W_2} \times 100 \quad (2)$$

where W_1 , W_0 , and W_2 denote, respectively, the weight of the grafted chitosan, the weight of original chitosan, and the weight of the monomer used.

Table 1
Details of the dyes

Dye	CI name	Type	λ (nm)	Absorbance (50 ppm)	Solution pH
Procion Yellow MX 8G (yellow)	Reactive Yellow 86 C.I. 192755	1,3-Benzene disulfonic acid	416.94	1.7	7
Remazol Brilliant Violet (violet)	Reactive Violet 5R C.I. no 18097	Vinyl sulfone	560, 325	0.7, 0.6	7
Reactive Blue H5G (blue)	C.I. Reactive Blue 81	5-Amino-2-anilinobenzene-sulfonic acid	660, 619.5	1.1, 1.0	4

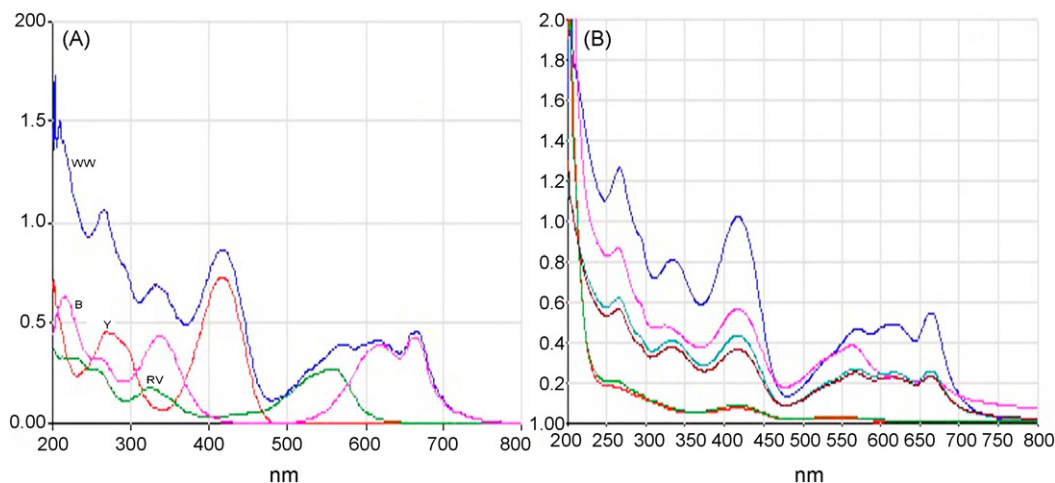


Fig. 2. (A) Spectrum of dyes: WW (spiked wastewater); Y (yellow); B (blue); V (violet). (B) Spiked wastewater after treatment with varying doses of Ch-g-MMA.

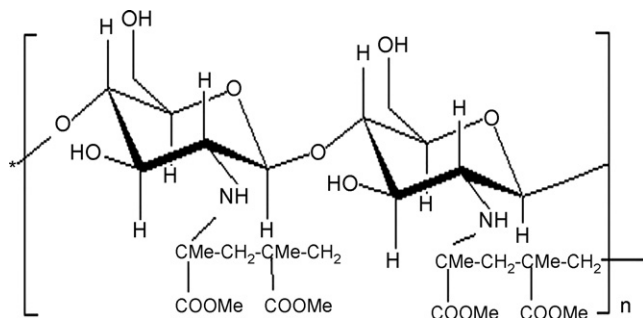


Fig. 3. Structure of Ch-g-PMMA.

Table 2

%G and %E at different monomer concentrations: [AA] = 2.3×10^{-2} M; $[K_2S_2O_8] = 1.0 \times 10^{-2}$ M; Chitosan = 0.1 g, total volume 25 mL, 35 ± 0.2 °C

S. no.	[MMA] in M	%G	%E
1	11×10^{-2}	48	17.45
2	15×10^{-2}	55	14.66
3	19×10^{-2}	62	13.03
4	23×10^{-2}	85	14.76
5	27×10^{-2}	105	15.53

2.3. 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 Isodebexlex 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

Table 3

%G and %E at different $[K_2S_2O_8]$ concentrations: [AA] = 2.3×10^{-2} M; [MMA] = 27×10^{-2} M; Chitosan = 0.1 g, total volume 25 mL, 35 ± 0.2 °C

S. no.	$[K_2S_2O_8]$ in M	%G	%E
1	1.0×10^{-2}	105	15.53
2	1.5×10^{-2}	123	18.20
3	2.0×10^{-2}	146	21.60
4	2.5×10^{-2}	172	25.45
5	3.0×10^{-2}	195	28.85

Table 4

%G and %E at different [Ascorbic acid] concentrations: $[K_2S_2O_8] = 3.0 \times 10^{-3}$ M; [MMA] = 27×10^{-2} M; Chitosan = 0.1 g, total volume 25 mL, 35 ± 0.2 °C

S. no.	[Ascorbic acid] in M	%G	%E
1	2.3×10^{-2}	195	28.85
2	2.7×10^{-2}	207	30.62
3	3.1×10^{-2}	216	31.96
4	3.4×10^{-2}	222	32.84
5	3.7×10^{-2}	226	33.44

maximum absorbance (λ_{max}) using a visible spectrophotometer (Systronics model 105). COD was measured using APHA method [22]. 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 was measured using microprocessor conductivity meter (EISCO 1601). ^{13}C NMR has been performed of sample on DSX-300 MHz FT-NMR spectrometer for solids.

2.4. Dye adsorption batch experiments

Adsorption experiments were carried out using the copolymer sample of 250% grafting (maximum) as adsorbent on a temperature controlled incubator shaker set at 120 rpm maintained at 30 °C for 3 h. A known amount of adsorbent was thoroughly mixed with 20 cm³ of respective dye solutions, whose concentration and pH were previously known. pH of the reaction mixture was initially adjusted using either hydrochloric acid or sodium hydroxide (1 M). No significant change in λ_{max} of the 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.

Table 5

%G and %E at different temperatures: $[K_2S_2O_8] = 3.0 \times 10^{-3}$ M; [MMA] = 27×10^{-2} M; [AA] = 3.7×10^{-2} M, Chitosan = 0.1 g, total volume 25 mL, 35 ± 0.2 °C

S. no.	Temperature in °C	%G	%E
1	30	185	27.37
2	35	226	33.44
3	40	238	35.21
4	45	250	36.99
5	50	210	31.07

For the optimization of the adsorption, one parameter was varied at a time keeping the others fixed. For pH studies, 20 cm³ of 100 ppm dye solutions were adjusted to various pH ranging from 2 to 10 and the optimum pH was determined using 50 mg adsorbent dose. Various doses of the modified adsorbent ranging from 25 to 125 mg were used to study the effect of adsorbent dose on the adsorption of the dyes at 100 mg L⁻¹ concentrations. The effect of temperature on the sorption of dyes was studied from 20–50 °C at 500 ppm dye concentration using 50 mg adsorbent dose. To study the effect of dye concentration, the range for different initial concentrations of dyes used was 100–1000 ppm at 50 mg adsorbent dose. In order to evaluate kinetic data, the agitation time was varied from 30 min to 6 h and the kinetic studies were done at 500 mg L⁻¹ dye concentration and 50 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 100 ppm dye concentration, 50 mg adsorbent dose, 20 cm³ working volume, 120 rpm and 3 h shaking time. The amount of dye adsorbed by the adsorbent from the spectrophotometer reading of equilibrium solution was calculated using the following equation.

$$q_e(\text{mg g}^{-1}) = C_0 - C_e(\text{mg L}^{-1}) \times \frac{V(\text{L})}{W(\text{g})} \quad (3)$$

where q_e is the amount of the dye adsorbed (mg g⁻¹) on the adsorbent, C_0 is the initial concentration of dye (mg L⁻¹), C_e is the equilibrium concentration of dye in solution (mg L⁻¹), V is the volume of the dye solution used (L), and W is the weight of the adsorbent used (g).

The industrial textile wastewater was spiked with a known amount of the mixture of the three dyes. A slight λ_{max} shift was observed for violet (567, 328) and Blue (665.4, 614) dyes (Fig. 2A). The adsorption of the mixture of the three dyes onto the adsorbents was studied using the ADMI (American Dye Manufacturer Institute) method [22] both at pH 4 and 7. This method is applicable to colored waters and wastewaters having color characteristic. In the batch experiments, the spiked wastewater and 50 mg adsorbent were shaken in the shaker at 120 rpm and maintained at 30 °C for 3 h. Concentrated HCl was used to maintain the dye solution at pH 4. At regular intervals, 0.10 cm³ 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 400–700 nm after the pH of diluted residual solution was adjusted to desired pH.

3. Results and discussions

Well documented K₂S₂O₈/ascorbic acid redox initiator was used for the grafting of methylmethacrylate on to chitosan. The adsorbent synthesis was optimized by varying one parameter at a time: concentration of MMA, chitosan, persulfate, ascorbic acid or the reaction temperature. Optimum grafting yield was obtained at [K₂S₂O₈] = 3.0 × 10⁻³ M; [MMA] = 27 × 10⁻² M; [AA] = 3.7 × 10⁻² M; chitosan = 0.1 g; total volume 25 cm³, 35 ± 0.2 °C (Tables 2–5). Thus, K₂S₂O₈/ascorbic acid redox initiator could be successfully used for the grafting of methylmethacrylate on to chitosan. The representative graft copolymer (250% G) sample was characterized by FTIR, XRD and ¹³C NMR.

3.1. Characterization of the Ch-g-PMMA and dye loaded Ch-g-PMMA

The IR spectrum of the parent chitosan showed strong peaks at 1030, 1081, and 1254 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 was assigned to the stretching vibration of O–H, extension vibration of N–H and intermolecular hydrogen bonds of the polysaccharide (Fig. 4). The IR spectrum of Ch-g-PMMA had additional sharp absorption peaks at 1733, 2952 and 2997 cm⁻¹ due to carbonyl stretching and symmetrical and asymmetrical stretching of the methyl group respectively. This provided a substantial evidence of grafting of PMMA on to the chitosan. To separate the PMMA grafts from the chitosan backbone, the graft copolymer was subjected to acid hydrolysis. The FTIR spectrum of the dried product obtained after acid hydrolysis of Ch-g-PMMA was identical to that reported for the PMMA, which further confirmed the formation of Ch-g-PMMA.

A broad crystalline peak at 2- θ 21° is observed in chitosan while after PMMA grafting, it acquires crystalline areas around 2- θ 28° and 31–32° (Fig. 5). Change in XRD pattern evidenced the grafting

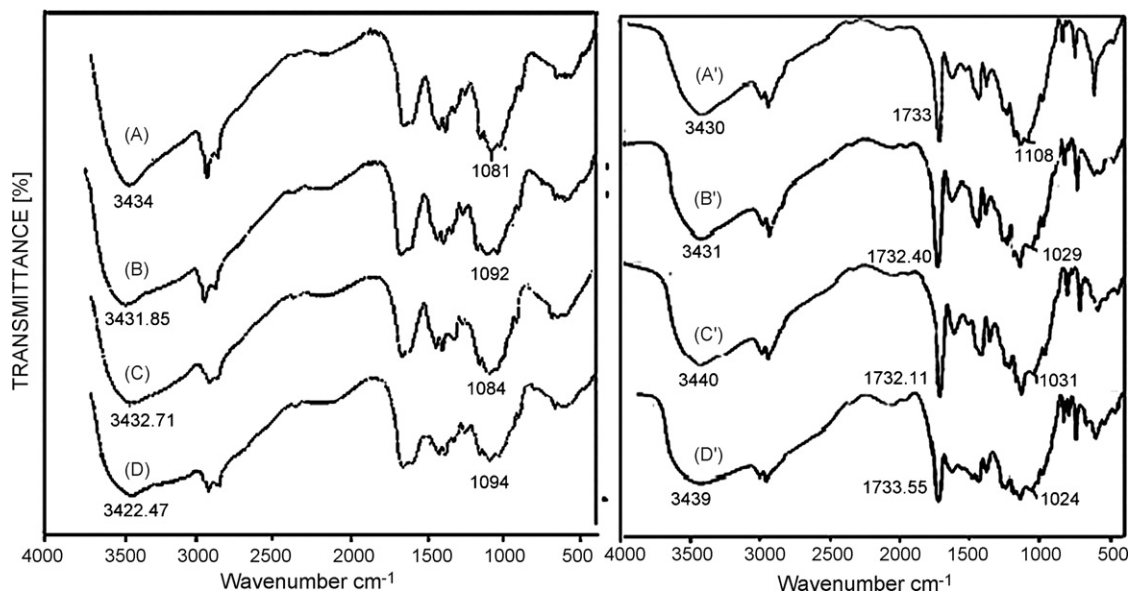


Fig. 4. IR spectra of Ch and Ch-g-PMMA and dye loaded Ch and Ch-g-PMMA. (A) Chitosan; (B) Ch – blue dye; (C) Ch – violet dye; (D) Ch – yellow dye. (A') Ch-g-PMMA; (B') Ch-g-PMMA – blue dye; (C') Ch-g-PMMA – violet dye; (D') Ch-g-PMMA – Yellow dye.

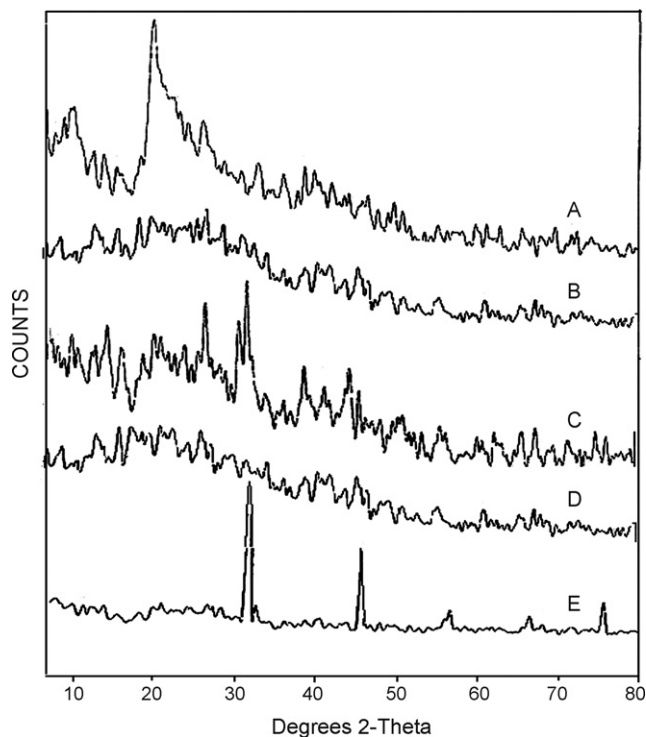


Fig. 5. XRD of Ch (A); Ch – blue dye (B); Ch-g-PMMA (C); Ch-g-PMMA – blue dye (D); blue dye (E).

of PMMA on to chitosan. However XRD pattern of the dyes shows their nature to be crystalline.

Solid-state ^{13}C NMR spectrum of the copolymer further confirmed the formation of the graft copolymer (Fig. 6). Due to PMMA grafts in the copolymer the peaks are seen at δ 179.882 ppm (C=O carbon of PMMA grafts); δ 17.465 (α -methyl of the PMMA grafts); δ 46.532 (quaternary carbons of PMMA grafts); δ 53.615 ($-\text{CH}_2$ of grafts); while peaks at δ 112.374, δ 106.36 and δ 76.568 are due to anomeric carbons, carbons attached to amino group and other carbons of the polysaccharide molecule, respectively.

The changes in the FTIR spectrum of the adsorbent after binding with the dye were significant. In chitosan, the N–H and O–H stretching observed as broad and strong peak at 3434.80 cm^{-1} , shifted to 3431.85 , 3432.71 and 3422.47 cm^{-1} after binding in case

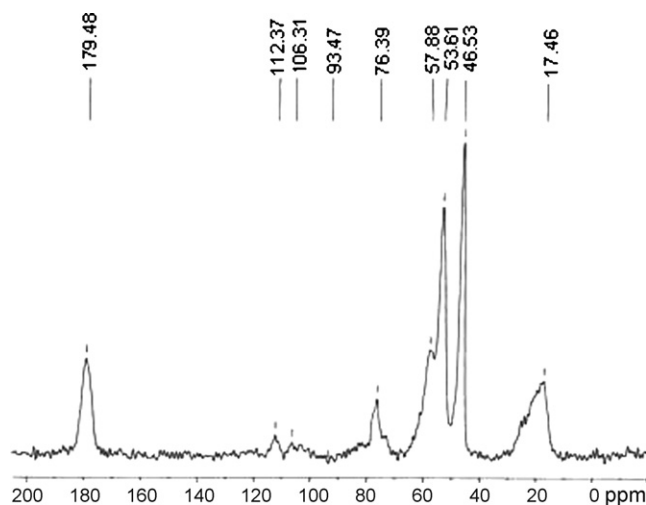


Fig. 6. ^{13}C NMR of Ch-g-PMMA.

of blue, violet and yellow dye, respectively. A slight shift in N–H bending vibrations of chitosan (at 1653.66 cm^{-1}) was also observed for all the dyes after adsorption. C–N stretching (at 1081 cm^{-1}) in chitosan shifted to 1092.50 , 1084.89 and 1094.89 cm^{-1} after interaction with blue, violet and yellow dye, respectively.

IR spectra of Ch-g-PMMA and dye loaded Ch-g-PMMA (Fig. 4) revealed that PMMA grafts and the available ungrafted NH_2 groups are the binding sites in the graft copolymer. In Ch-g-PMMA, N–H and O–H stretching peaks merge to give broad strong peak at 3430.74 cm^{-1} , which after dye interaction are seen shifted to 3431.49 , 3440.63 and 3439.53 cm^{-1} for the blue, violet and yellow dye, respectively. N–H wagging in Ch-g-PMMA shifted to 618 cm^{-1} due to intramolecular hydrogen bonding with PMMA grafts present at the copolymer. The intensity of this peak was significantly reduced after interaction with the dyes. The C=O and $-(\text{C=O})-\text{O}$ stretching, seen at 1733.00 and 1244.09 cm^{-1} , respectively in the copolymer were shifted slightly after the dye interaction. The $-\text{O}-\text{C}-\text{C}-$ stretching in Ch-g-PMMA, seen at 1108 cm^{-1} , shifted to 1029.64 cm^{-1} in blue dye, 1031 cm^{-1} in violet dye and to 1024 cm^{-1} in yellow dye indicating the participation of PMMA grafts of the copolymer in the binding.

The structure of the dyes played an important role in the adsorption process. In some dyes the slow decolorization rate could be attributed to the complexity of their chromophores, but the overall complexity alone is not an indicator of the difficulty of decolorization of a particular dye [23,24]. Even small structural differences can affect the decolorization process. It was observed that compared to the disulfonic dyes (blue and yellow), the dye with a vinyl sulfone chromophore (violet), was much easier to remove via binding with the adsorbent.

The XRD pattern of the dyes shows their nature to be crystalline but the dye loaded chitosan and Ch-g-PMMA showed a totally amorphous character. Change in XRD pattern of the Ch-g-PMMA after dye interaction is thus observed.

3.2. Sorption kinetics

% Removal of dye at a fixed adsorbent dose was monitored with time. The kinetics of dye removal by Ch-g-PMMA indicated rapid binding of dye to the sorbent during first few minutes, followed by a slow increase until a state of equilibrium at 3 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 was an increased concentration gradient between adsorbate in solution and adsorbate in the adsorbent [25]. 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. (2)–(4), respectively.

$$\frac{\text{Log}(q_e - q_t)}{q_e} = \frac{\text{Log } q_e - K_L t}{2.303} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k' q_e^2} + \frac{t}{q_e} \quad (3)$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (4)$$

where K_L is the Lagergren rate constant of adsorption (min^{-1}); k' is the pseudo-second-order rate constant of adsorption ($\text{g mg}^{-1} \text{min}^{-1}$) and K_2 is the second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$); q_e and q_t are the amounts of dye adsorbed (mg g^{-1}) at equilibrium and at time t , respectively. The adsorption kinetic

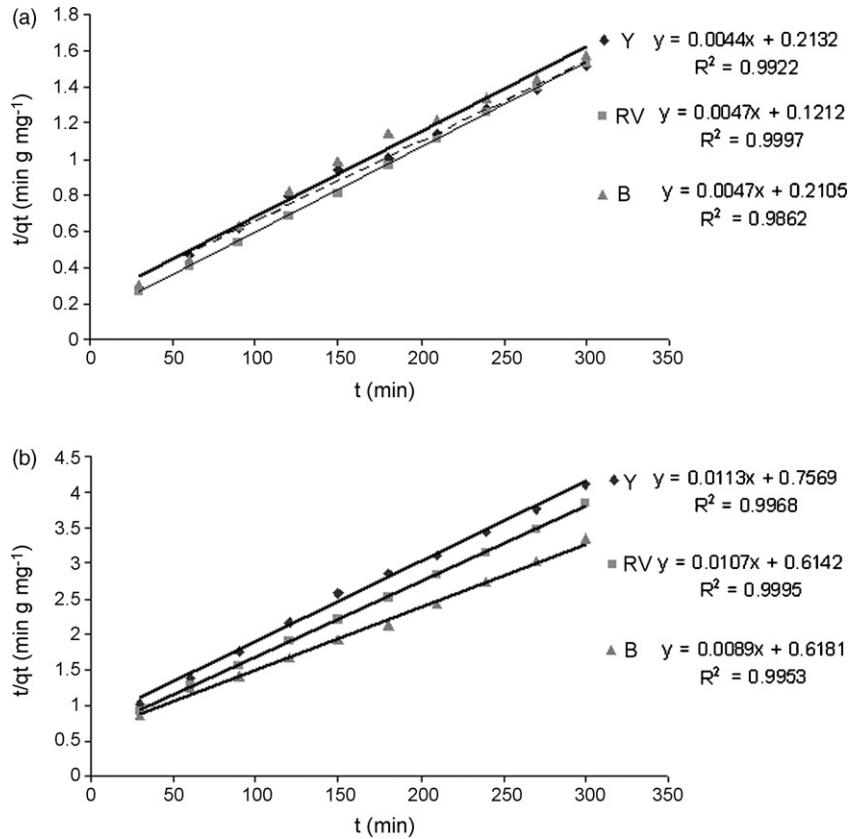


Fig. 7. (a) Pseudo-second-order kinetics of Ch-g-PMMA adsorption of the dyes at 500 ppm dye concentration, adsorbent dose = 50 mg, pH 7.0, reaction volume = 20 ml, rpm = 120 at 30 °C. (b) Pseudo-second-order kinetics of chitosan adsorption of the dyes at 500 ppm dye concentration, adsorbent dose = 50 mg, pH 7.0, reaction volume = 20 ml, rpm = 120 at 30 °C.

data (at pH 7.0) of both, Ch-g-PMMA and chitosan were modeled by Lagergren equation, the pseudo-second-order equation and the second-order rate equation, where for both the adsorbents the data fit best in pseudo-second-order model (Fig. 7a and b), where linear plots of t vs t/qt were obtained. The correlation coefficients (R^2) and the rate constants for chitosan and Ch-g-PMMA are summarized in Table 6. These results suggest that adsorption kinetics of the dye molecules are not diffusion controlled, but chemisorption.

3.3. Optimization of sorption

3.3.1. Effect of % grafting

Grafting plays a significant role in increasing the efficiency of the grafted adsorbent as evident from Fig. 8. With increase in % grafting from 50 to 250, there was an increase in the adsorption for all the three dyes. Initial increase in %G (from 50–200%G) had greater influence on the sorption thereafter the increase was nominal.

3.3.2. 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. Most of the dyes are ionic and upon dissociation conferred dye ions into solution. The degree of adsorption of these ions onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which in turn is influenced by the solution pH [26]. 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 [27]. The effect of pH on dye removal by Ch and Ch-g-PMMA is shown in Fig. 9a. It was observed that percentage removal of dye by Ch-g-PMMA was almost constant for over a wide pH range, though the adsorption was lesser at pH 2 for violet and yellow dyes. Lower adsorption at acidic pH ($pH < pH_{zpc}$) is probably due to the presence of excess H^+ ions competing with the cation groups on the dye for adsorption sites. However with increase in pH from 4 to

Table 6
Sorption kinetics of the dyes by Ch-g-PMMA and chitosan

Dye	Lagergren plot		Pseudo-second-order		Second-order	
	R^2	K_L	R^2	K'	R^2	K
Ch-g-PMMA						
Yellow	0.9179	3.0×10^{-5}	0.9922	0.91×10^{-4}	0.5542	13.0×10^{-4}
Violet	0.7664	2.0×10^{-5}	0.9997	1.82×10^{-4}	0.7607	7.0×10^{-4}
Blue	0.9431	2.0×10^{-5}	0.9862	1.05×10^{-4}	0.7859	3.0×10^{-6}
Sorption kinetics of the dyes by Chitosan						
Yellow	0.9292	2.0×10^{-6}	0.9968	1.68×10^{-4}	0.9494	7.0×10^{-6}
Violet	0.8840	2.0×10^{-6}	0.9995	1.86×10^{-4}	0.9089	8.0×10^{-6}
Blue	0.8725	3.0×10^{-6}	0.9953	1.28×10^{-4}	0.8982	10.0×10^{-6}

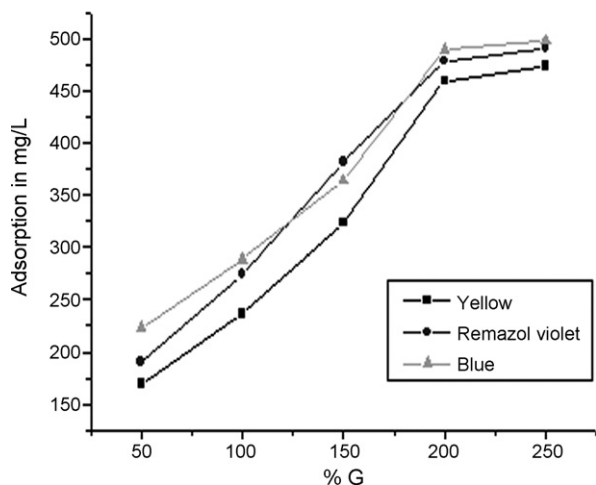


Fig. 8. Adsorption of different dyes using samples of different %G, at pH 7.0, dye concentration = 500 ppm, adsorbent dose = 50 mg, rpm = 120, contact time = 3 h.

pH 10, for all the three dyes (at 100 ppm dye concentration, 50 mg adsorbent dose) the increase in % removal ranged from 92% to 99%. Even on increasing the concentration of dye to 500 ppm, a similar adsorption trend was observed for all the dyes, indicating that the effect of pH variation on the adsorption of the dyes is concentration independent. However for chitosan, adsorption was found pH dependent and was maximum at pH 4 (62.75% for yellow; 72.88 for violet and 89.72% for blue). As surface charge density decreases with an increase in the solution pH ($pH > p_{H_{zpc}}$), the electrostatic repulsion between the positively charged dyes and the surface of the chitosan is lowered, which may result in an increase in the rate of adsorption. In the case of chitosan the adsorption of

dyes occurs by the conversion of pH of the carbon surface higher than $p_{H_{zpc}}$ whereas in the case of Ch-g-PMMA this was not the dominating factor. In the grafted polymer, it appears that the carbonyl group of PMMA does not participate much rather it is the ester $-O-C-C$ bond which is taking part in the binding with the dyes.

It was observed that at acidic and alkaline pH of the dye solution the initial pH changed with time during the adsorption process until equilibrium. The trend was such as to attain neutral pH values toward equilibrium as depicted in Fig. 9b. However, at the initial pH 7.0, there was no change in pH during adsorption and it remained fixed. Since at pH 7, no variation in pH was observed during adsorption and the adsorption results (for Ch-g-PMMA) were slightly better, the optimization of adsorption by the copolymer was done at pH 7.

3.3.3. 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 Ch-g-PMMA are shown in Fig. 10. With the increase in the initial concentration of dye from 100 to 800 mg/L at 120 rpm, 30 °C, 50 mg adsorbent dose, the percentage removal increased initially but after 400 ppm dye concentration, adsorption of the blue dye declined significantly, while adsorption for the other two dyes decreased slowly. The decrease in adsorption with increase in dye concentration is more marked at pH 7 than at pH 4. At lower concentrations, all sorbate ions present in the adsorption medium could interact with the binding sites, hence higher dye % uptake. At higher concentrations, because of the saturation of the adsorption sites, the % uptake of the dyes by the copolymer showed a decreasing trend.

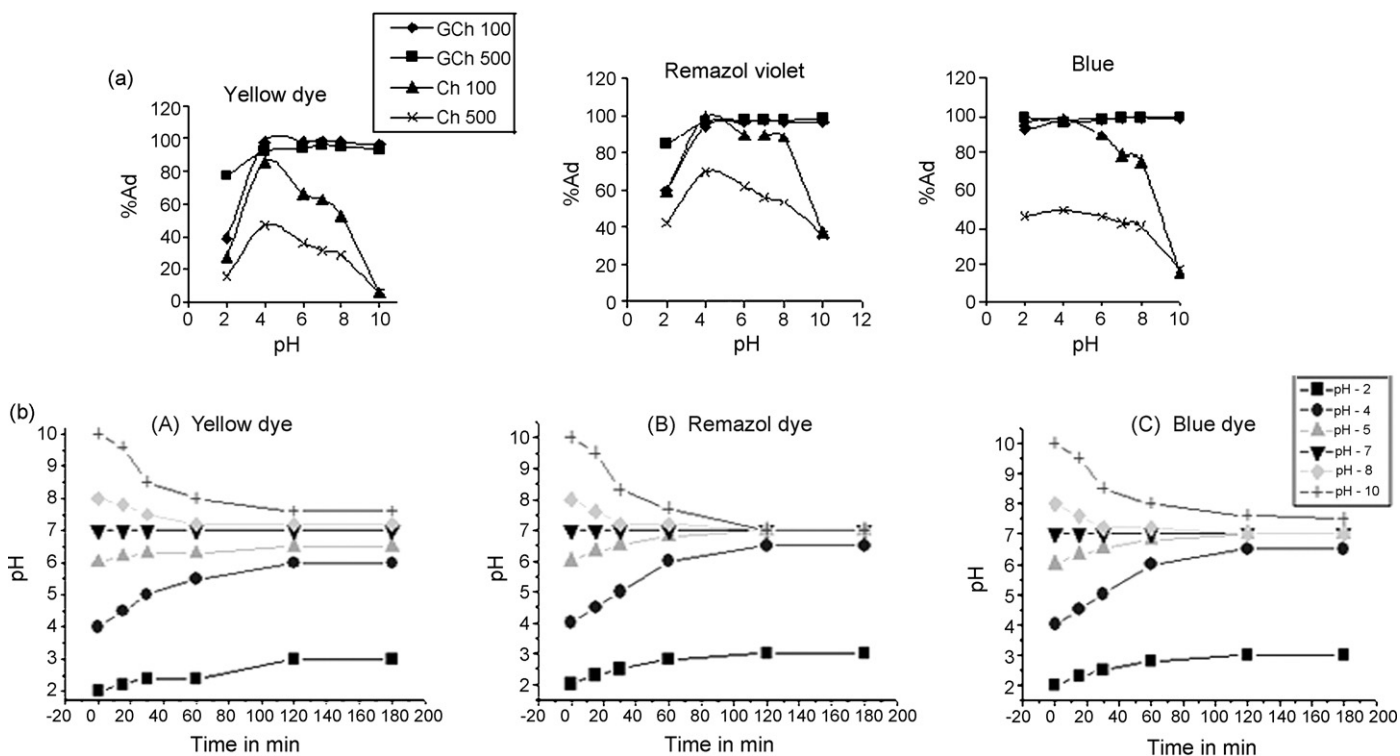


Fig. 9. (a) Adsorption of different dyes (500 ppm concentration = Y axis) at different pH. (b) Changes in initial pH of dyes with time (A) yellow dye; (B) Remazol dye; (C) blue dye.

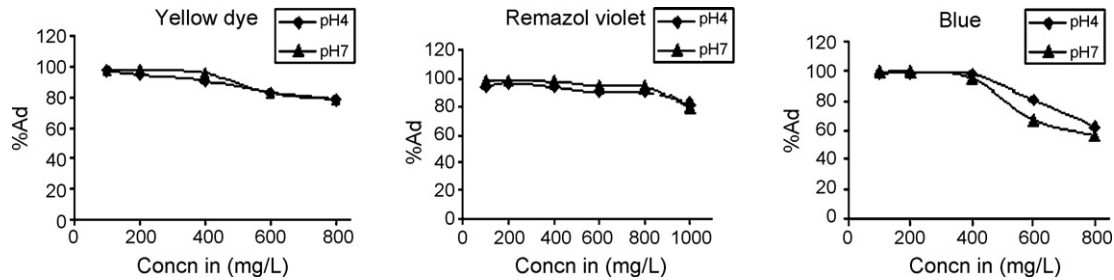


Fig. 10. % Adsorption of yellow, violet and blue dyes by Ch-g-PMMA at different dye concentration at 50 mg adsorbent dose.

3.3.4. Effect of adsorbent amount

In order to study the effect of adsorbent dosage on dye removal, various amounts of the grafted copolymer (25–125 mg) were contacted with a fixed initial dye concentration of 1000 ppm. It was observed that for all the three dyes on increasing the adsorbent dose, % removal increased. With increase in the adsorbent dose, additional sorbent sites are available for the adsorption and hence removal of dye molecules from the solution is increased (Fig. 11). 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.

3.3.5. Effect of temperature

The effect of increasing temperature on the sorption was studied in the range of 20–50 °C at 500 ppm dye concentration using 50 mg adsorbent dose at pH 4.0 and 7.0. It was observed with increase in the temperature, sorption for all the three dyes increased (Fig. 12a), indicating endothermic nature of the adsorption. The increase in the adsorption with temperature can be partly attributed to the increase in the chemical potential of the chitosan with temperature, however a detailed investigation is required for fully understanding the issue. At pH 4, a sharp increase in adsorption for yellow dye was observed on increasing the temperature from 20 to 30 °C, whereas for violet and blue dyes increase in the adsorption was very nominal. Adsorption of violet and blue dyes increased significantly when the temperature was raised from 40 to 50 °C. At pH 7.0, with increase in temperature from 20 to 30 °C, an initial sharp increase in adsorption was observed for all the three dyes, which slowly stabilized and remained almost constant with further increase in the temperature from 30 to 50 °C (Fig. 12).

3.4. Thermodynamic studies

The thermodynamic parameters including change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), were determined by using Van't Hoff equation [28].

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

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

$$\Delta G^\circ = -\frac{2.303 RT \log C_{ac}}{C_{eq}}$$

The values are listed in Table 7. Effect of temperature on the adsorption process is shown in Fig. 12b where $\log C_{ac}/C_{eq}$ (K_C) is plotted against $1/T$ and ΔH° and ΔS° are obtained according to Van't Hoff equation [28]. Where K_C is the equilibrium constant, C_{ac} is the amount of the dye adsorbed on the adsorbent at equilibrium (mg/l), C_e is the equilibrium concentration of the dye in the solution (mg/l), R is the gas constant and T is the temperature in Kelvin.

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-PMMA indicating some chemical binding between the dye and the adsorbent material. As $\Delta H^\circ > 0$ i.e. higher temperature will facilitate the adsorption of dye onto Ch-g-PMMA. 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.

3.5. 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 in the linear form as under

$$\frac{C_e}{q_e} = \frac{b}{Q_0} + \frac{C_e}{Q_0} \quad (5)$$

where C_e is the equilibrium concentration (mg L^{-1}) and q_e is the amount adsorbed at equilibrium (mg g^{-1}). The Langmuir constants Q_0 (mg g^{-1}) represent the monolayer adsorption capacity and b (L mg^{-1}) relates the heat of adsorption. The essential feature of the

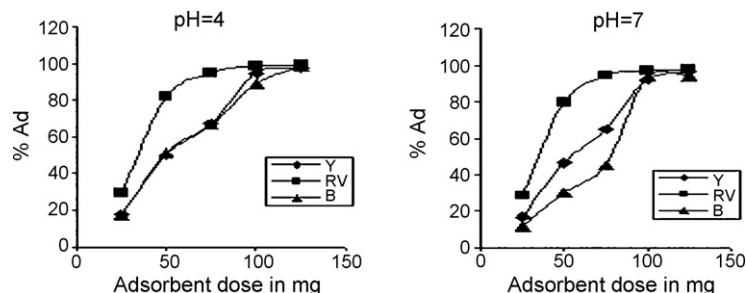


Fig. 11. % Adsorption of yellow, violet and blue dyes by Ch-g-PMMA at different adsorbent dose at 1000 ppm dye concentration.

Table 7
Thermodynamic parameters for the adsorption of the dyes on to Ch-g-PMMA

Dyes	Temperature (K)	pH 7			pH 4		
		ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol)
Yellow	293	-5.29	+32.7	+0.131	-4.98	+24.02	+0.099
	303	-8.16			-6.23		
	313	-8.66			-7.13		
	323	-9.43			-7.97		
Violet	293	-6.28	+49.5	+0.193	-8.35	+33.78	+0.141
	303	-10.16			-8.77		
	313	-11.11			-9.19		
	323	-12.28			-13.08		
Blue	293	-5.73	+113.0	+0.41	-7.55	+84.45	+0.309
	303	-14.03			-8.40		
	313	-15.92			-9.97		
	323	-18.55			-17.64		

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

$$R_L = \frac{1}{(1 + bC_0)} \quad (6)$$

where C_0 is the initial dye concentration (mg L^{-1}). If R_L values lie 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:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (7)$$

where K_f indicates adsorption capacity (mg g^{-1}) and n an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. The greater is the values of the n , better is the favorability of the adsorption.

Adsorption data, both at pH 4 and 7 (for chitosan and Ch-g-PMMA) were modeled using both the Langmuir and Freundlich isotherms where the data fitted better to Langmuir isotherm

indicating surface homogeneity of the adsorbent and unilayer adsorption. Langmuir and Freundlich isotherm constants at pH 7.0 for the dyes are compared in Table 8, Fig. 13.

Q_m and b values in the adsorption by Ch-g-PMMA and chitosan are listed in Table 9. It was observed that at both pH Q_m values are higher for Ch-g-PMMA than chitosan for all the three dyes. Q_m values of some reported biosorbents are also listed in Table 10.

3.6. Adsorption mechanism

The anionic dye, bearing sulfonic groups, is electrostatically attracted by protonated amine groups of the chitosan, thus neu-

Table 8
Langmuir and Freundlich isotherm constants at pH 7.0 for the dye

Dye	Langmuir isotherm			Freundlich isotherm		
	Q_{\max}	b (L mg^{-1})	R^2	n	K_f (mg g^{-1})	R^2
Yellow	250	0.0782	0.9917	2.89	265.1	0.8621
Violet	357	0.0567	0.9980	2.32	287.5	0.8646
Blue	178	0.2710	0.9961	5.52	421.0	0.7932

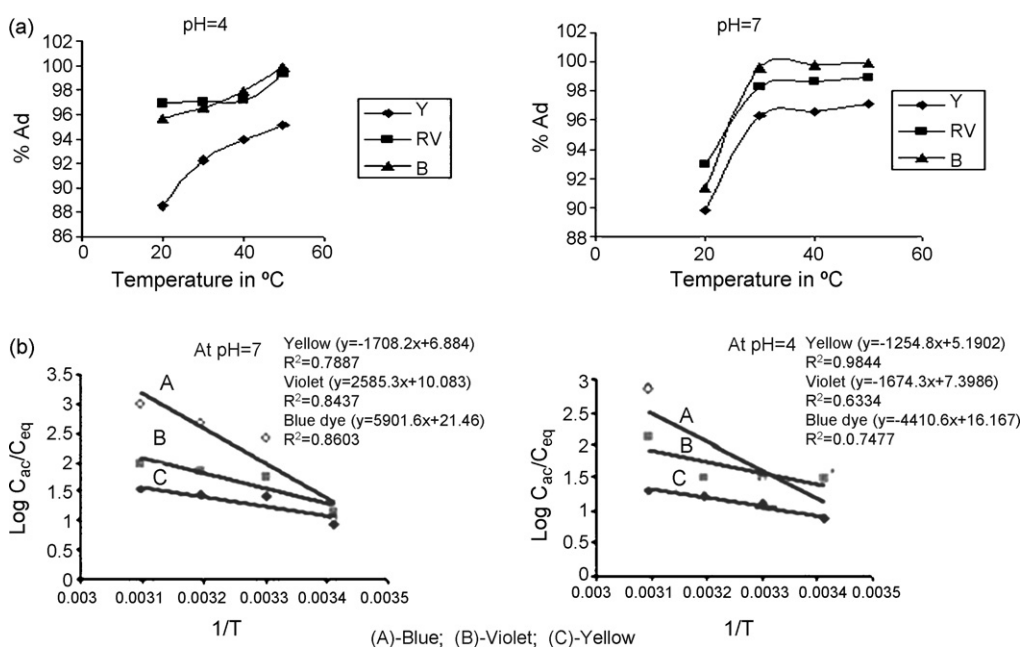


Fig. 12. (a) Adsorption of different dyes (500 ppm concentration = Y axis) by Ch-g-PMMA at different temperature. (b) Thermodynamic modeling of the adsorption of dyes at pH 7 by Ch-g-PMMA.

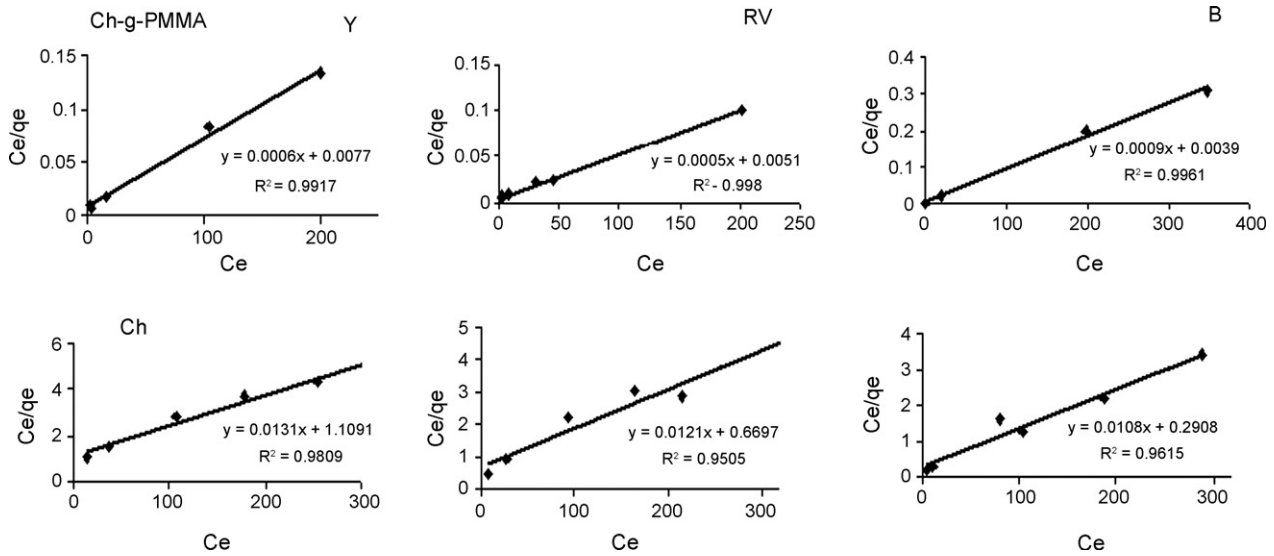


Fig. 13. Langmuir adsorption isotherms of adsorption by chitosan and Ch-g-PMMA for (A) yellow, (B) violet and (C) blue dye at pH 7.

Table 9

Q_m and b values of Ch-g-PMMA and Chitosan at pH 7.0 and pH 4.0

Adsorbent	Dye	pH 7.0		pH 4.0	
		Q_m (mg/g)	b (L mg ⁻¹)	Q_m (mg/g)	b (L mg ⁻¹)
Ch-g-PMMA	Yellow	250	0.0782	263	0.0342
	Violet	357	0.5670	384	0.0299
	Blue	178	0.2710	204	0.2150
Chitosan	Yellow	76	0.0110	126	1.0050
	Violet	82	0.0180	122	0.9996
	Blue	92	0.0371	123	1.0037

tralizing the anionic charges of dyes that can bind together. The removal of the dye reached a maximum at pH 4 with the complete neutralization of the anionic charges. However with increasing pH, deprotonation at amino group takes place that results in poor interaction between the dye and the biopolymer and therefore

the decrease in adsorption. On the other hand at much acidic pH (pH < 4), protonation takes place at the nitrogens (N=N; NH) and carbonyl groups present in the dyes which decrease the adsorption due to electrostatic repulsion between the same charges. However in Ch-g-PMMA the dangling ester groups at the grafted chitosan appear to be mainly responsible for the adsorption and not the amino groups as is also evident by IR spectrum of dye loaded adsorbent. Also, other than electrostatic interaction some interaction in the form of conformational affects may also be operative. The sensitivity to pH after pH 4 is not seen in the graft copolymer because the major binding takes place at PMMA grafts and only a very small amount of NH₂ are available for binding after grafting for binding.

3.7. Removal of color from real wastewater

The wastewater from textile industry usually contains a mixture of many dyes and other toxic contaminants which may interfere or

Table 10

Some recently reported high maximum sorption capacity (q_m) of dyes for some non-conventional adsorbents

S. no.	Adsorbent	Q_{max} (mg g ⁻¹)	pH	Dyes	Reference
1	Wheat bran	69.06	5.6	Astrazon Yellow 7GL	[30]
2	Calcium alginate beads	57.70	4.0	Basic black dye	[31]
3	Native and heat-treated Fungal biomass	101.1 and 152.3	6	Direct Blue 1	[32]
4	Carbon prepared from silk cotton hull	12.9	3	Direct Red 128	[33]
5	Carbon prepared from rattan sawdust	294.14	2	Reactive blue MR	[34]
6	Carbon obtained from <i>Euphorbia rigida</i>	114.45	–	Methylene blue dye	[35]
7	Palm ash	400.01	6	Methylene blue	[36]
8	Leather waste	80	7.0	Direct blue 71	[37]
9	Coal-based bottom ash	163	7.0	Dye methylene blue	[37]
10	Cyclodextrin-based material	6.35	7	Reactive red	[38]
11	Poly(γ -glutamic acid)	91.9	8	Vertigo Navy Marine	[38]
12	Chitosan hydrobeads	277.29	5	Malachite Green	[14]
13	Chitosan	390.25	5	Auramine O	[8]
14	PMMA grafted Chitosan	502.83	6	Rhodamine B	[17]
		93	4	Safranin	[17]
		75	6	Congo red	[17]
		156	4	Eosin Y	[17]
		277	10	Reactive Red 141	[39]
		384	4.0	Procion Yellow MX 8G	This Study
		204	4.0	Remazol Brilliant Violet	This Study
		250	7.0	Reactive Blue H5G	This Study
		357	7.0	Procion Yellow MX 8G	This Study
		178	7.0	Remazol Brilliant Violet	This Study
				Reactive Blue H5G	This Study

Table 11
Adsorption from mixture of dyes by Chitosan and Ch-g-PMMA at pH 4.0, adsorbent dose 50 mg

Concentration (mg L ⁻¹) of the three dyes	λ_{\max} 416 nm (yellow)		λ_{\max} 560 nm (violet)		λ_{\max} 619.12 nm (blue)	
	Ch	Ch-g-PMMA	Ch	Ch-g-PMMA	Ch	Ch-g-PMMA
50 + 50 + 50	36.26	48.37	36.98	48.85	32.50	49.17
100 + 100 + 100	59.65	98.09	70.83	98.50	56.80	99.12
200 + 200 + 200	93.00	188.20	94.70	181.30	90.40	190.40
300 + 300 + 300	141.90	254.80	123.50	241.10	147.50	247.50
400 + 400 + 400	221.04	361.90	207.40	345.50	180.30	351.80

Table 12
Adsorption from wastewater spiked with mixture of dyes (100 ppm each)

Polymer	Adsorption at pH 4.0			Adsorption at pH 7.0		
	Yellow	Violet	Blue	Yellow	Violet	Blue
Chitosan (50 mg)	45.2	51.54	43.5	13.06	24.7	19.7
Chitosan (100 mg)	62.4	85.20	86.08	16.09	39.7	38.30
Ch-g-PMMA (50 mg)	78.87	92.20	95.22	19.09	38.68	43.7
Ch-g-PMMA (100 mg)	84.71	96.00	97.50	30.06	67.80	72.3

hinder the efficiency of the adsorbents. To study the effect of other contaminants (present in the wastewater) on the adsorption behavior of the adsorbents, a ternary mixture of dyes (each dye in equal concentration), was spiked in real textile wastewater (Table 11). The adsorption of mixture of the three anionic dyes onto chitosan (at pH 4) and Ch-g-PMMA (both at pH 4 and 7) were studied by ADMI [29] 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. The adsorption % of each single dye with the same initial concentrations as those in mixture solution was also measured for comparisons. When a ternary mixture of synthetic dye (200 ppm each) solution was used instead of a single dye of a particular concentration (e.g. 200 ppm), the adsorption efficiency of the adsorbents showed a slight dip. For chitosan it was 93 from 93.7 for yellow, 94.7 from 106.2 for violet, 90.4 from 121.3 for blue and for Ch-g-PMMA it was 188 from 196.8 for yellow, 181 from 197 for violet 190 from 199 for blue.

Structurally different dyes were not decolorized to the same extent. The azo dyes, due to their chemical structure, are not readily degradable and are considered to be resistant to decolorization. The differences between decolorization of structurally different dyes are not easy to explain [30]. When the same ternary mixture of dyes was spiked in the real wastewater the efficiency of the adsorbents was further reduced to some extent (Table 12) due to the presence of some other interfering anions. However for the industrial wastewater, both chitosan and Ch-g-PMMA worked better at pH 4 than at pH 7.

4. Conclusions

Ch-g-PMMA proved to be a much better adsorbent than chitosan in the removal of anionic dyes from synthetic dye solutions as well as from real textile wastewater. Unlike chitosan which worked best at pH 4, Ch-g-PMMA was found to be very efficient over a wide pH range of 4–10 where pH change had negligible effect on the adsorption. The adsorption was found dependent on concentration and temperature of the dye solutions. Equilibrium adsorptions of dyes in synthetic solutions were attained in about 3 h. For all the three dyes the adsorption followed pseudo-second-order kinetic model, suggesting chemisorption. Depending on the structure of the dyes the adsorbent affinity towards the dyes was in the order violet > yellow > blue for both chitosan and Ch-g-PMMA.

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