

Cassia fistula seed gum-graft - poly(acrylamide): An efficient adsorbent for reactive blue H5G dye

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ABSTRACT

Poly(acrylamide) has been efficiently grafted onto *Cassia fistula* seed gum using ceric ammonium sulphate/sodium disulphite redox system. The conditions for obtaining optimum % grafting (208 %) and % efficiency (92 %) are: acrylamide = 0.16 M, ceric ammonium sulphate = 0.026 M, sodium disulphite = 0.050 M, *Cassia fistula* seed gum = 25 mL (0.4 % (w/v)), and temperature = 40 ± 0.2 °C. *Cassia fistula*-graft-poly(acrylamide) (CF-g-PAM) was characterized using FTIR and SEM studies. CF-g-PAM could very efficiently capture “Reactive Blue (RB_{H5G})” dye from its aqueous solution. The copolymer did not dissolve even under highly acidic pH conditions and was able to remove 99.4 % dye from 100 mg L⁻¹ dye solution under the optimized conditions (pH= 2, rpm = 150, adsorbent dose = 30 mg, temperature = 40 °C, and contact time = 4 h). The adsorption equilibrium data are better explained by Freundlich isotherm, which indicated the presence of heterogeneous adsorption surface sites at CF-g-PAM. Langmuir adsorption isotherm, indicated significantly high Q_{\max} (500 mg g⁻¹) for the adsorption. The dye adsorption followed a pseudo second order kinetics ($k' = 5.3 \times 10^{-3}$ g. mg⁻¹ min⁻¹), indicating chemisorption of the dye is taking place. The kinetic study also supported the intervention of some boundary layer control. The results revealed that ceric ammonium sulphate/and sodium disulphite redox system is an efficient system for grafting poly(acrylamide) onto *Cassia fistula* seed gum and CF-g-PAM behaved as an efficacious adsorbent for Reactive Blue H5G dye. In future, the material may be explored for the adsorption of other anionic azo dyes and may be developed as the proficient dye adsorbent. Copyright © 2016 VBRI Press.

Keywords: *Cassia fistula* seed gum; poly(acrylamide); grafting; reactive blue dye; adsorption.

Introduction

Water pollution is a serious issue for all the developing countries. Industries such as textile, paper, printing, cosmetics, plastics, and rubber [1] are discharging their toxic effluents to the water bodies. These effluents mainly contain heavy metals, aromatic compounds, and dyes. Most of the commercial industrial dyes are synthetic in nature and possess complex and stable aromatic compounds [2]. The remediation of dye-containing effluents is essential [3, 4] they are known to have carcinogenic and mutagenic effects on the living systems [5].

Many physical and chemical methods of dye removal are in practice such as ion exchange, chelation, precipitation, ozonolysis, and adsorption [4, 7, 8]. Most of these dye remediation techniques involve high running cost, labour-intensive operation, and low removal efficiency [9]. The dye removal using adsorption is most attractive among the available methods as it involves simple design and low operational cost. Dye adsorbents derived from natural resources [10-14] are in high demand as they are nontoxic and cost effective. Polysaccharide based adsorbents, in particular derived from chitin [15], chitosan [16-18], starch, [19] and cyclodextrin [20] have emerged as good

alternatives to the conventional adsorbents. Seed gums from leguminous plants are attractive and abundant natural materials for deriving dye adsorbents. They can be easily modified due to their multifunctional nature. *Cassia* is a common annual plant grown in tropical countries and is abundantly available throughout India. The galactomannan from *Cassia javahikai* seed gum and its graft copolymer have been utilized for coagulating the textile wastewater [21].

Cassia fistula is widely distributed medicinal plant which is cultivated as ornamental plant in tropical and subtropical areas. Its seeds contain a gum which is structurally related to guar gum [22]. Guar gum and its many derivatives have been utilized in dye remediation [23-25] processes. *Cassia fistula* seed gum is attractive scaffold for deriving dye adsorbent due to its abundant nature, low cost and structural resemblance to guar gum.

Many poly(acrylamide) derivatives [26-27] are reported to be effective in dye removal from aqueous solution. In the present study we have targeted the synthesis of efficacious dye adsorbent by poly(acrylamide) modification of *Cassia fistula* seed gum. The copolymer has been evaluated for the removal of reactive azo dyes by taking “Reactive Blue H5G” (RB_{H5G}) as a model azo dye. RB_{H5G} dye is a hazardous but frequently used industrial azo dye. To

understand the adsorption behaviour of the copolymer, and for a breakthrough in its utilization as adsorbent, the conditions for the adsorption have been optimized. The kinetic and the adsorption equilibrium studies have also been performed. *Cassia fistula*-graft-poly(acrylamide) proved to be a highly efficient and low cost effective dye adsorbent material. It may be exploited for the remediation of dye rich industrial effluents. This is the first report regarding the utilization of *Cassia fistula* seed gum for dye removal.

Experimental

Materials

Acrylamide (Merck, India) was recrystallized with methanol before use. Sodium disulfite and ceric ammonium sulfate (Merck, India) were used without further purification. Deionized water was used throughout the study. *Cassia fistula* seed gum was supplied by Himani seed stores, Dehradun and identified by systematic botanist at Botanical Survey of India, Allahabad. The reactive blue (H5G) dye (Megha International, Maharashtra, India) was used without further purification. Dye stock solution was prepared by dissolving 5 g of RB_{H5G} dye in 1 L of double distilled deionized water. The pH values were adjusted with the help of 5 M HCl (GR, Merck, India, 35%); or 1 M NaOH (Merck, India).

Instrumentation

EUTECH Instruments pH meter (model 510) was used for the pH measurements. Orbital shaker Incubator, (Metrex Scientific Instruments (P) Ltd., New Delhi) was used for the adsorption experiments. Scanning Electron Microscopy (SEM) was employed to observe microscopic morphology of the copolymer using FEI ESEM QUANTA 200 instrument with an accelerating voltage of 25 kV. The samples were gold coated to avoid charging. Perkin Elmer Infrared spectrophotometer (version 10.03.06) was used for the FTIR study. The FTIR spectra were recorded on KBr pellets. UV/Vis Spectrophotometer UV 100, (Cyber lab, USA) was used to determine the dye concentrations in the solutions at $\lambda = 619$ nm. The percentage of the colour removal was calculated by comparing the absorbance of the supernatant to the standard curve that was obtained from known dye concentrations.

Isolation of the seed gum

Cassia fistula (CF) seeds (1 kg) were exhaustively extracted with light petroleum and EtOH to remove the fatty and colouring materials respectively. The mucilage extracted from the defatted and decolorized seeds (using 1% acetic acid (v/v)) was precipitated in 95% EtOH to obtain the seed gum [22].

Purification of the seed gum

The gum was purified through barium complexing for which 2.5% (w/v) solution of the gum was precipitated with saturated barium hydroxide solution. The complex was separated by centrifugation and taken in 1 M CH₃COOH, stirred for 8 h, centrifuged, and precipitated with EtOH. It

was washed sequentially with 70, 80, 90, and 95 % ethanol. The sample was finally purified by dialysis and filtration through millipore membranes. The pure seed gum thus obtained was a non-reducing, white, and fibrous material.

Synthesis of *cassia fistula* gum-graft-poly(acrylamide) (adsorbent)

A calculated amount of acrylamide (AA) and ceric ammonium sulfate (CAS) were added to 25 mL of CF seed gum solution of known concentration, and the reaction mixture was thermostated at a known temperature [28]. After 30 min, a calculated amount of sodium disulfite was added and the time of addition of disulfite was taken as zero time. Graft copolymerization was allowed for 1 h. Grafted CF gum samples (of different % grafting) were separated by pouring the respective reaction mixtures into excess of methanol-water (7:3). CF-g-PAM samples were finally extracted with methanol-water in a soxhlet apparatus for 4 h to remove the adhered homopolymer if any. CF-g-PAM samples were finally dried under vacuum at 50 °C for >24 h to a constant weight. % Grafting and % Efficiency (% G and % E %) were calculated [28] using the Eqs. (1) and (2).

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

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

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

Dye adsorption batch experiments

RB_{H5G} dye stock solution was diluted with deionized distilled water to obtain the dye solutions of required initial concentrations (50 to 300 mg L⁻¹). The details of the dye are given in **Table 1**. Sample having maximum % G was used as adsorbent for the batch adsorption experiments. Adsorption experiments were carried out on a temperature controlled incubator shaker set at a known rpm (Rate of stirring at definite number of rounds per minute) and temperature for a known time period. The batch adsorption study was performed at different pH, initial dye concentration, adsorbent dose, and contact time to optimize the adsorption conditions.

Table 1. Details of the Reactive blue dye.

Dye	C.I. Name	Type	λ (nm)	Absorbance (50 mg/L)	Solution pH
Reactive Blue H5G (blue)	C.I. Reactive Blue 81	5-Amino-2-anilinobenzene-sulfonic acid	660, 619.5	1.1, 1.0	4

A known amount of adsorbent was thoroughly mixed with 20 mL of the dye solution whose concentration and pH were previously known. After the flask was shaken for the desired time period, the suspension was filtered through

filter paper and the filtrate was analyzed for the residual dye concentration. The adsorption experiment was also performed using the native gum under the identical experimental conditions but it fully dissolved during the experiment. Control experiments did not reveal any sorption on either the glassware or the filtration systems used.

The dye adsorption was optimized by varying one adsorption process parameter while keeping the others fixed. To study the effect of pH on the dye adsorption, 20 mL of 100 mg L⁻¹ dye solutions were adjusted to various pH values (ranging from pH 2 to 10). The dye was found to be soluble and stable in the pH range of 2-12. The batch adsorption experiments were performed using 20 mg adsorbent (CF-g-PAM), 100 rpm, 4 h contact time, and 40 °C temperature. Effect of rpm was studied using 20 mg adsorbent dose, 20 mL contact volume, 100 mg L⁻¹ initial dye concentration, pH 2, contact time 4 h, and temperature 40 °C. The effect of contact time was monitored for 30 to 360 min for 100 mg L⁻¹ initial dye concentration using 20 mg CF-g-PAM dose, 100 rpm, pH 2, and temperature 40°C. Separate flasks were prepared for each time interval and only one flask was taken for the desired time. Various weights of the adsorbent ranging from 10 to 50 mg were used to study the effect of CF-g-PAM dose at 100 mg L⁻¹ initial dye concentration, pH 2, 150 rpm, 4 h contact time, and temperature 40°C. The effect of temperature on the sorption was studied from 20 to 50°C at 100 mg L⁻¹ initial dye concentration, 30 mg adsorbent dose, 20 mL contact volume, pH 2, 150 rpm, and contact time 4 h. Effect of initial concentration was studied using 30 mg CF-g-PAM; 20 mL contact volume, pH 2, 150 rpm, 4 h contact time, and 40 °C temperature.

The adsorption isotherms were studied at two temperatures (20°C and 30°C) using 30 mg adsorbent dose, 20 mL contact volume, pH 2, rpm 150, and contact time 4 h. The kinetic study was done at 100 mg L⁻¹ initial dye concentration, adsorbent dose = 20 mg, pH = 2, contact volume = 20 mL, rpm = 150 at 30 °C.

The equilibrium dye concentration (after the adsorption) and the initial dye concentration were determined spectrophotometrically and the amount of the dye adsorbed on CF-g-PAM was calculated by using the equation 3.

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

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

Desorption studies

The dye desorption from the loaded CF-g-PAM was attempted in order to determine the reusability of the copolymer. To explore the possibility of adsorbent recovery for the recycling, the spent adsorbent was stirred separately with distilled water, 1 N HCl, 1 N H₂SO₄ and 1 M NaOH (2 h each). As the effective dye stripping could be achieved with NaOH, the concentration of the NaOH was varied

from 0.01 to 1M to obtain the best results. The quantitative stripping could be obtained with 0.1 M NaOH.

Dye loaded CF-g-PAM samples were placed in the 0.1 M NaOH and stirred at 150 rpm for 2 h at 40°C and the final dye concentration was determined. After each cycle the used CF-g-PAM was washed with distilled water and reused in the succeeding cycle. The amount of the desorbed dye was calculated from the amount of dye loaded on the copolymer and the final dye concentration in the stripping medium. For the quantitative stripping, 2 h of equilibration time was sufficient. Each sample was used thrice after the successive leaching. In the recycling experiments, an adsorbent dose of 20 mg was used for 20 mL of 100 mg L⁻¹ dye solution.

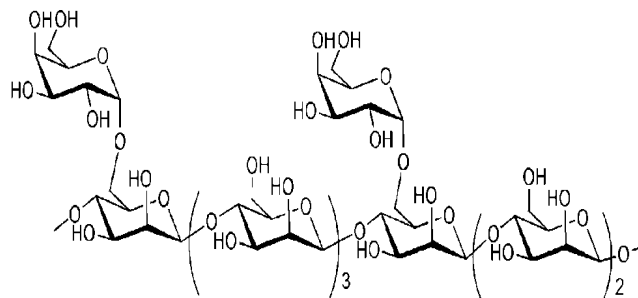


Fig. 1. Repeating unit structure of CF polysaccharide.

Results and discussion

Cassia fistula seed gum is a water soluble galactomannan polysaccharide having galactose and mannose units in the average molar ratio of 1:3.5 [22] (Fig. 1). The seed gum possesses metal ion chelating cis hydroxyl groups at the mannose residues of its backbone. The water solubility of the seed gum was altered by grafting poly(acrylamide) onto the seed gum backbone. A redox system consisting of ceric ammonium sulphate/sodium disulfite was used for the grafting and the involved process parameters were optimized to achieve optimal % G and % E.

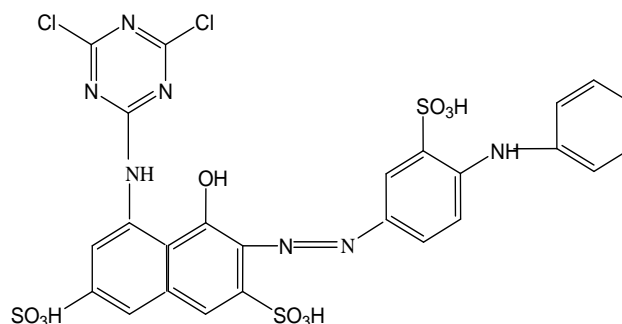


Fig. 2. Chemical Structure of the RBH5G dye.

All the synthesized samples of the CF-g-PAM were evaluated for their efficiency in RBH5G dye removal. The synthetic conditions for obtaining the optimum performance sample are: 0.1 g CF gum, 0.026 M CAS, 0.05 M sodium disulfite, 0.16 M AA at 40 °C (Table 2). The grafted seed gum was water insoluble and was efficient in capturing anionic dye molecules (Fig. 2) due to the added amide functionality in the graft chains.

Optimization of the grafting conditions

The various process parameters such as the concentration of acrylamide, sodium disulfite, ceric ammonium sulfate, CF gum, and the grafting temperature were varied one at a time to optimize the grafting of PAM onto CF gum. The grafting time and total reaction volume were kept fixed at 1 h and 25 mL respectively for all the experiments. The maximum % G and % E that could be achieved are 208 % and 92 %, respectively (**Table 2**).

Table 2. Optimization of the CF-g-PAM synthesis.

Sl. No.	Temp (°C)	CF Gum (% w/v)	CAS [M]	Na ₂ S ₂ O ₅ [M]	AA [M]	% G [%]	% E [%]
1.	35	0.4	0.011	0.03	0.08	35	31
	35	0.4	0.011	0.03	0.10	47	33
	35	0.4	0.011	0.03	0.12	55	32
	35	0.4	0.011	0.03	0.14	67	34
	35	0.4	0.011	0.03	0.16	80	35
2.	35	0.4	0.011	0.010	0.16	65	28
	35	0.4	0.011	0.020	0.16	78	34
	35	0.4	0.011	0.030	0.16	87	38
	35	0.4	0.011	0.040	0.16	98	43
	35	0.4	0.011	0.050	0.16	120	53
3.	35	0.4	0.006	0.050	0.16	50	22
	35	0.4	0.011	0.050	0.16	85	37
	35	0.4	0.016	0.050	0.16	110	48
	35	0.4	0.021	0.050	0.16	145	64
	35	0.4	0.026	0.050	0.16	180	79
4.	35	0.4	0.026	0.050	0.16	180	79
	35	0.6	0.026	0.050	0.16	160	70
	35	0.8	0.026	0.050	0.16	100	44
	35	1.0	0.026	0.050	0.16	80	35
	35	1.2	0.026	0.050	0.16	65	29
5.	30	0.4	0.026	0.050	0.16	130	57
	35	0.4	0.026	0.050	0.16	175	77
	40	0.4	0.026	0.050	0.16	208	92
	45	0.4	0.026	0.050	0.16	205	90
	50	0.4	0.026	0.050	0.16	205	90

Effect of monomer concentration

% G and % E increased from 35% to 80% and 31% to 35% respectively on increasing the monomer concentration from 0.08 to 0.16 M at fixed concentrations of ceric ammonium sulphate (0.011 M), sodium disulfite (0.03 M), CF gum (0.4 % (w/v)) in a total reaction volume of 25 mL at 35 °C. This increase can be assigned to the generation of additional grafting sites at high monomer concentration due to the formation of extra monomer free radicals (Mn*).

Effect of sodium disulfite concentration

Both % G and % E were increased on increasing disulfite concentration from 0.01 M to 0.05 M at 0.16 M acrylamide, 0.011 M ceric ammonium sulfate, 0.4 % (w/v) CF gum, 25 mL total reaction volume, and 35 °C temperature. % G and % E were maximum (120% and 53% respectively) at 0.05 M disulfite concentration, indicating that at this concentration the grafting takes place immediately after the activation along the backbone.

Effect of ceric ammonium sulfate concentration

The effect of ceric ammonium sulfate (CAS) was studied in the concentration range 0.006–0.026 M at 0.16 M acrylamide, 0.05 M, sodium disulfite, 0.4 % (w/v) CF gum, 25 mL total reaction volume, and 35 °C temperatures. Increase in the % G and % E (50 % to 180 %, and 22 % to 79 % respectively) with the increase in [CAS] may be due to the generation of more primary free radicals that in turn generated extra grafting sites.

Effect of gum concentration

The effect of gum concentration was studied in the concentration range of 0.4–1.2 % w/v. CF gum solution (25 mL) of different concentrations were used with 0.05 M sodium disulfite, 0.026 M ceric ammonium sulphate, and 0.016 M acrylamide at 35 °C. % G and % E decreased (180 to 65% and 79 to 29% respectively) as the gum concentration was increased, the decrease may be attributed to the increased viscosity of the reaction medium at high gum concentrations and also because of the decrease in the monomer/polysaccharide ratio.

Effect of temperature

The grafting reaction was carried out at different temperatures (30–50°C) at 0.05 M sodium disulfite; 0.026 M ceric ammonium sulphate; 0.16 M acrylamide (0.16 M), and 0.4 % (w/v) CF gum solution, 25 mL total reaction volume. The maximum % G was obtained at 40°C temperature. Increase in % G (130 % to 208 %) and % E (57% to 92 %) with increase in temperature from 30 to 40°C may be attributed to the increase in the number of collisions between the monomer and the gum molecules and because of the decrease in the viscosity of the reaction medium at higher temperature. Further increase in temperature (45 °C) decreased % G and % E that may be due to increase in the homopolymerization.

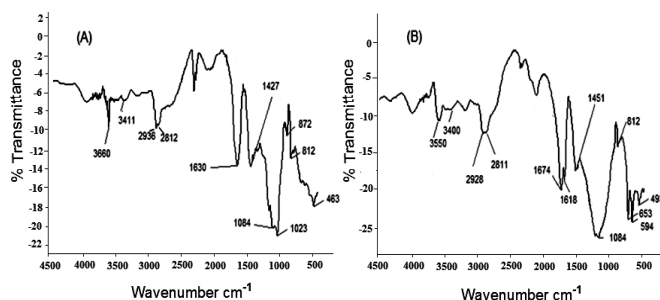


Fig. 3. FTIR of (A) *Cassia fistula* seed gum; (B) CF-g-PAM.

Characterization of the CF-graft-poly(acrylamide)

Fourier transform infrared spectroscopy

The IR spectra of the CF gum and CF-g-PAM are shown in **Fig. 3**. The IR spectrum of the CF gum showed O–H stretching peak at 3411 cm⁻¹ while C–H stretching peaks are seen at 2936 cm⁻¹ and 2812 cm⁻¹ respectively. The strong sharp peak at 1630 cm⁻¹ can be assigned to the ring stretching [29]. The strong peaks in the region of 1200–900 cm⁻¹ can be assigned to the finger print of

carbohydrates [30]. C-O stretching is visible at 1084 cm^{-1} . The IR spectrum of CF-g-PAM showed additional peaks at 1674 (Amide I) and 1618 cm^{-1} (Amide-II) due to the presence of PAM graft chains at CF seed gum, while peaks of O-H and N-H stretching in the grafted CF gum are seen at 3550 cm^{-1} , 3400 cm^{-1} and 3330 cm^{-1} respectively.

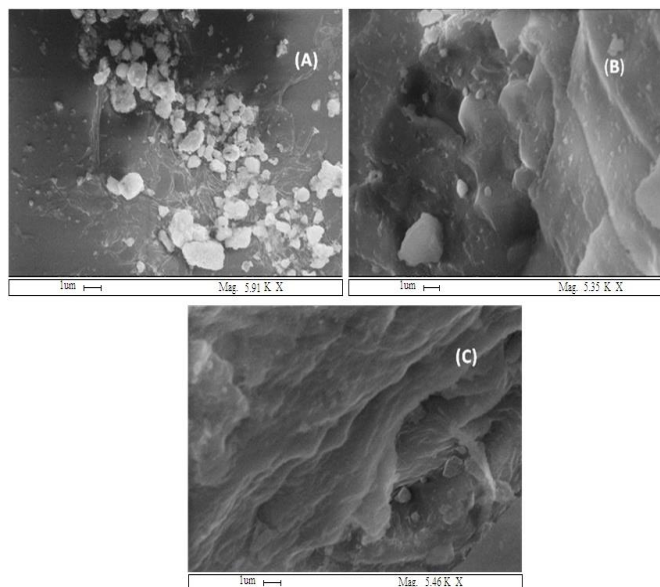


Fig. 4. SEM picture of CF gum (A); CF-g-PAM (B); Dye loaded CF-g-PAM.

Scanning electron microscopy

SEM picture of *Cassia fistula* seed gum, CF-g-PAM and dye loaded CF-g-PAM are shown in **Fig. 4**. The native gum appeared to be made up of irregular shaped bulk particles, while the CF-g-PAM showed lamellar flattened porous surface topology. The dye loaded CF-g-PAM showed different surface morphology as it reflects fine layered structure (**Fig. 4(C)**).

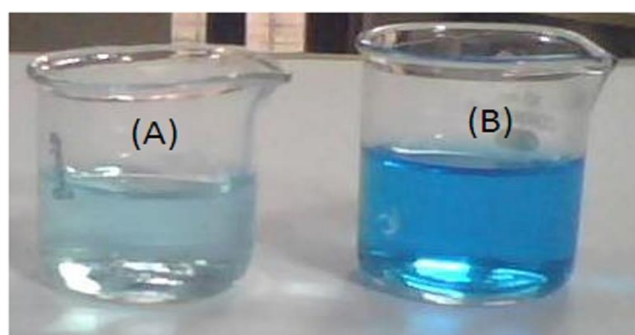


Fig. 5. Dye removal under optimized conditions (A) after removal (B) before removal.

Optimization of dye removal

The dye removal was optimized by changing the process parameters of the batch adsorption experiments. The CF-g-PAM could capture 99.4 % dye from 100 mg L^{-1} synthetic dye solution under the optimized conditions (pH= 2, rpm = 150, adsorbent dose = 30 mg, temperature = $40\text{ }^{\circ}\text{C}$, and contact time = 4 h) (**Fig. 5**).

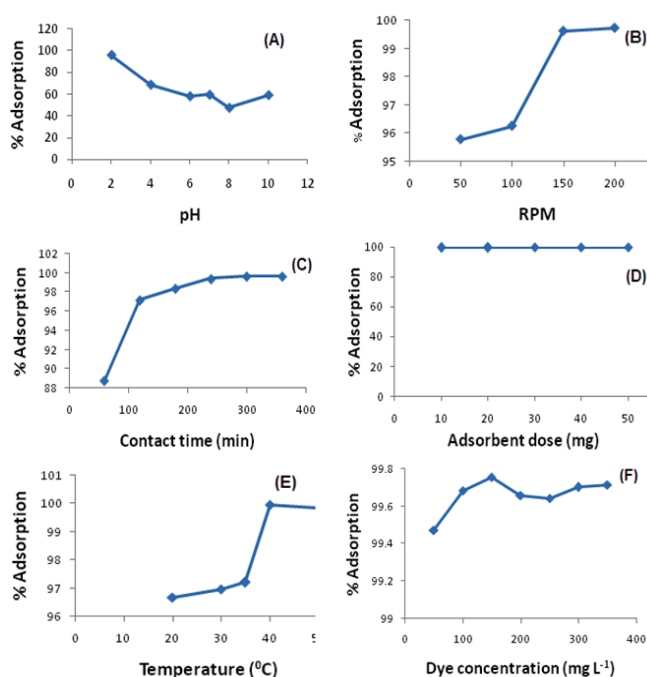


Fig. 6. Optimization of dye adsorption: (A) Effect of pH: CF-g-PAM (20 mg); contact volume = 20 mL; initial dye concentration = 100 mg L^{-1} , contact time = 4 h, rpm = 100, temperature = $40\text{ }^{\circ}\text{C}$; (B) Effect of rpm: CF-g-PAM = 20 mg; contact volume = 20 mL; initial dye concentration = 100 mg L^{-1} , pH = 2, contact time = 4 h; temperature = $40\text{ }^{\circ}\text{C}$; (C) Effect of contact time: initial dye concentration = 100 mg L^{-1} , CF-g-PAM dose = 20 mg; pH = 2, rpm = 150, temperature = $40\text{ }^{\circ}\text{C}$; contact volume = 20 mL; (D) Effect of Adsorbent dose: contact volume = 20 mL; initial dye concentration = 100 mg L^{-1} , pH = 2, rpm = 150, contact time = 4 h; temperature = $40\text{ }^{\circ}\text{C}$; (E) Effect of temperature: CF-g-PAM dose = 30 mg; contact volume = 20 mL; initial concentration of the dye = 100 mg L^{-1} , pH = 2; rpm = 150; contact time = 4 h; (F) Effect of initial concentration of dye: CF-g-PAM = 30 mg; contact volume = 20 mL, pH = 2, rpm = 150 contact time = 4 h, temperature = $40\text{ }^{\circ}\text{C}$.

Effect of pH on the dye removal

The pH of the dye solution plays an important role in the whole adsorption process [31]. The effect of pH on Reactive Blue H₅G dye adsorption is shown in **Fig. 6 (A)**. Dye removal was monitored in the pH range of 2 to 10 at 100 mg L^{-1} initial dye concentration, 4 h contact time, 20 mg adsorbent dose, and $40\text{ }^{\circ}\text{C}$ temperature. CF-g-PAM showed best adsorption performance at pH 2. At acidic pH, the sulfonic acid bearing dye molecules are electrostatically attracted to the protonated amide/ hydroxyl groups of the copolymer (**Fig. 7**). As the pH of the dye solution was increased, the deprotonation at the copolymer backbone resulted into negative surface sites. The dye adsorption decreased as the negative surface of the copolymer now had a decreased interaction with the anionic azo dye molecules. It was observed that pH of the dye solution gradually increased during the adsorption process. The pH of the dye solution was raised to pH 4 after a contact time of 4 h. The gradual increase in the pH of the dye solution can be attributed to the electrostatic interaction between the anionic dye and the copolymer surface.

Effect of rpm

The effect of agitation speed was studied in the rpm range of 50–200 using 100 mg L^{-1} initial dye concentration, pH 2,

contact time 4 h, adsorbent dose 20 mg, and temperature 40 °C (**Fig. 6(B)**). The adsorption increased on increasing the agitation speed, and the highest adsorption was witnessed at 150 rpm. The increase in the adsorption with rpm can be attributed to the decrease in the thickness of the liquid boundary layer due to increased turbulence at the sorbent/sorbate interface. The adsorption decreased when the rpm was >150. This indicated that at such high rpm some desorption has taken place.

Effect of initial concentration of dye

The initial dye concentration decides mass transfer resistances of the dye between aqueous and solid phases. Dye removal was monitored at different initial dye concentrations (50-350 mg/L) at pH 2, 20 mg CF-g-PAM dose, 4 h contact time, 150 rpm and temperature 40 °C (**Fig. 6(C)**). The CF-g-PAM was shown to have high adsorption ability at pH 2 as it could constantly adsorb ~99 % of the dye over a concentration range of 50-350 mgL⁻¹. The final pH of the batch experiments was also monitored with time which gradually increased up to pH 4.

Effect of adsorbent amount

To study the effect of adsorbent dose on dye removal, the adsorbent dose ranging from 10 to 50 mg were contacted with 20 mL of 100 mgL⁻¹ dye solutions for 4 h (at pH 2, 150 rpm and 40 °C temperature). It was observed that on increasing the adsorbent dose, % removal of dye increased. An adsorbent dose of 40 mg was sufficient for almost complete adsorption of the dye. The dye adsorption increased with the adsorbent dose (**Fig. 6(D)**) as the additional sites now became available for the adsorption. The decrease in q_e with increase in the adsorbent loading can be attributed to the reduction in the quantity of dye adsorbed on to the unit weight of the adsorbent.

Effect of temperature

The effect of temperature on the dye adsorption was studied in the temperature range of 20–50 °C using 100 mg L⁻¹ initial dye concentration, 30 mg adsorbent dose, and pH 2.0. The adsorption increased from 96.4 % to 99.8 % as the temperature of the dye solution was raised from 20 to 50 °C. The increase in the adsorption with increase in temperature (**Fig. 6(E)**) is explainable since better interaction between the dye and the adsorbent molecules is possible due to the increased collisions at higher temperatures.

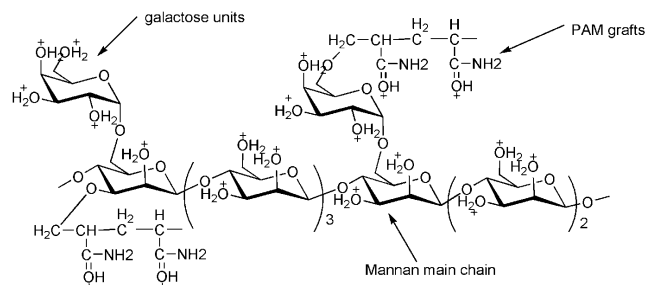


Fig. 7. CF-g-PAM at pH 2.

Adsorption mechanism

The pure CF gum was not suitable for dye adsorption due to its solubility in water whereas the CF-g-PAM was not only water insoluble but it also has extra binding sites at its porous lamellar structure (cf. SEM pictures). It is reported that the flattened and porous structure of a sorbent can provide additional binding-sites which amounts to extra adsorption [33, 34]. Nevertheless, grafted gum will also have stronger Van der Waals forces in comparison to the native gum [32] due to its higher molecular size. Functional groups like carboxyl, hydroxyl and amino groups are the preferred groups for most of the sorption processes [35, 36]. The dangling amide and hydroxyl groups at CF-g-PAM are the active centres for the sorption (**Fig. 7**). Thus, CF-g-PAM possesses all the characteristics that are needed for an efficient adsorbent. A diagrammatic scheme for the adsorbent synthesis and its application in the dye removal has been depicted in **Fig. 8**.

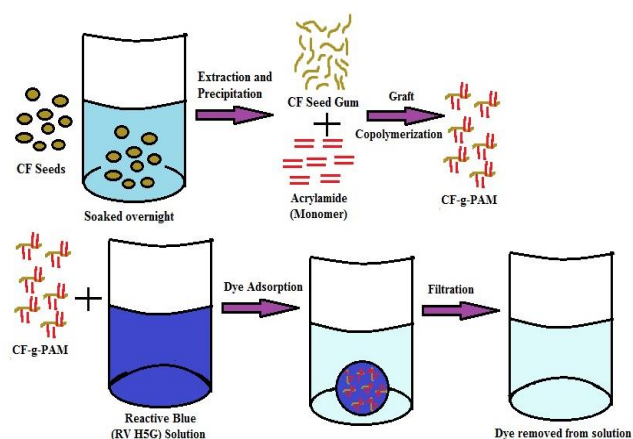


Fig. 8. Diagrammatic scheme of the Adsorption Process.

Adsorption kinetics

Kinetic analysis is required to understand any adsorption process and also for determining its rate limiting step. The study involves the monitoring of % dye removal with respect to time. The optimization study revealed that the dye adsorption was optimum at 40 °C. However, this temperature was not chosen for the kinetic and isotherm studies as the adsorption at this temperature was >99% in the studied concentration range.

Kinetics data were modeled by the first order Lagergren equation and the pseudo second-order equations (equations 4 & 5) at 30 °C. The possibility of intraparticle diffusion resistance that affects the adsorption was explored by using the intraparticle diffusion model (equation (6)).

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

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

$$q_t = k_p t^{1/2} + I \quad (6)$$

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_p ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the intraparticle diffusion constant, q_e and q_t are the amounts of dye adsorbed (mg g^{-1}) at equilibrium and at time t , respectively. The values of the rate constants, k_L , k' and k_p and the equilibrium dye uptake, q_e were obtained from the slope and intercepts of the plots obtained from the adsorption equilibrium data (Fig. 9).

Values of I give an idea about the thickness of the boundary layer, i. e; the larger is the intercept, the greater is the boundary layer effect. According to this model, the plot of uptake should be linear if intraparticle diffusion is involved in the adsorption process and if this line passes through the origin, then intraparticle diffusion is the rate controlling step [37-39]. When the plot does not pass through the origin, some degree of boundary layer control is assumed and the intraparticle diffusion is not the only rate limiting step. There are some other kinetic steps involved or all of them may be operating simultaneously.

The approaching equilibrium factor (R_w), which represents the characteristics of kinetic curve of an adsorption system is given by equation-7 [40].

$$R_w = \frac{1}{1+k'q_e t_{\text{ref}}} \quad (7)$$

where, t_{ref} is the longest operation time of kinetic experiments. The adsorption curve is called approaching equilibrium when R_w is in the range $0.1 < R_w < 1$; and it is well approaching equilibrium when R_w is in the range $0.01 < R_w < 0.1$; and it is drastically approaching equilibrium when $R_w < 0.01$.

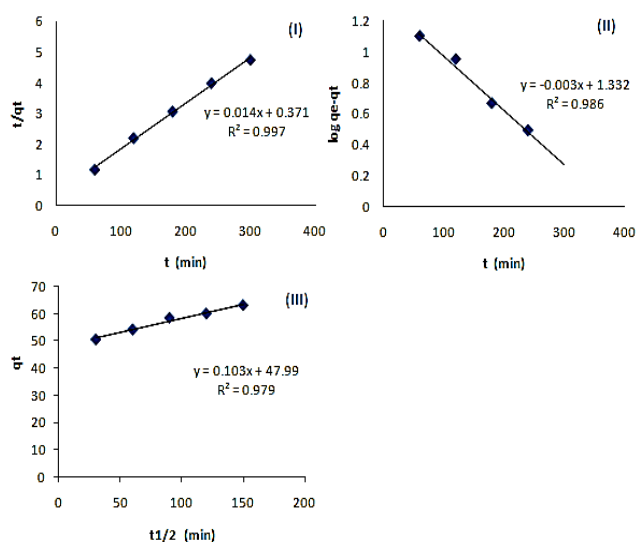


Fig. 9. Kinetic modelling [(I) Pseudo second order; (II) Lagergren first order, (III) Intraparticle diffusion] of the adsorption equilibrium data (CF-g-PAM = 20 mg, rpm = 150, initial dye concentration = 100 mg L⁻¹, contact volume = 20 mL, temperature = 30 °C).

It was observed that for first few minutes the dye sorption was rapid thereafter a gradual increase in sorption was noticed until a state of equilibrium was attained in 4 h. On further increasing the equilibration time (up to 24 h) no

change in the dye uptake was observed. The adsorption was rapid initially as in the beginning the adsorbent had a large number of vacant binding sites which established a high concentration gradient between the adsorbate in solution and in the adsorbent [41]. The adsorption sites gradually decreased with time and the dye adsorption eventually slowed down. Generally, when adsorption involves a surface reaction process, the initial adsorption is rapid.

The kinetics of the blue dye adsorption by CF-g-PAM was modelled by the pseudo-second-order equation, Lagergren equation, and Intra-particle diffusion model (Fig. 9). The linearity of the plots (R^2) demonstrated that pseudo second order and intraparticle diffusion kinetic models are applicable for the dye uptake by CF-g-PAM (Table 3). The linear fit between the t/q_t versus contact time (t) and calculated correlation coefficients (R^2) revealed that the dye removal kinetics can be approximated to pseudo-second order kinetic model (Table 3). The values of R_w indicate that the characteristic adsorption curve is well approaching equilibrium. High value of I indicate significant boundary layer effect. Since the line did not pass through the origin, the intraparticle diffusion is not the rate controlling step and there is some degree of boundary layer control while chemisorption is the rate determining step.

Table 3. Kinetic constants for dye adsorption onto CF-g-PAM at 30 °C (20 mL dye solution at initial dye concentration 100 mg L⁻¹ at pH=2, rpm=150).

Pseudo-second Order				Lagergren first order			Intraparticle diffusion		
q_e	k'	R_w	R^2	Q_e	k_L	R^2	k_d	I	R^2
71.42	5.3×10^{-4}	0.088	0.997	1.06	1.84×10^{-4}	0.987	10.3×10^{-2}	47.9	0.979

Adsorption isotherm study

Adsorption equilibrium data were fitted to the linear forms of Langmuir and Freundlich adsorption isotherm equations [42] which are expressed as equation (8) and equation (9) respectively.

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{bQ_0} \quad (8)$$

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

where, C_e is the equilibrium concentration (mg L^{-1}) and q_e is the amount of dye adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}). The Langmuir constant Q_0 is the maximum amount of dye adsorbed per unit weight of adsorbent to form a complete monolayer coverage (mg g^{-1}) and b is the Langmuir adsorption constant (Lmg^{-1}). K_f is the Freundlich adsorption constant which roughly indicates the adsorption capacity of the adsorbent and n is the Freundlich exponent which relates to the adsorption intensity. $1/n$ is a heterogeneity parameter, smaller the value of $1/n$, greater is the heterogeneity. The greater the value of $1/n$, better is the favourability of the adsorption. The higher fractional value of $1/n$ ($0 < 1/n < 1$) signifies that the surface of the adsorbent is heterogeneous in nature.

The affinity between the adsorbent and adsorbate can be calculated by substituting the value of Langmuir adsorption constant, b (L mg^{-1}) in the expression for the dimensionless separation factor, R_L , which is given by [40].

$$R_L = \frac{1}{1 + bC_0} \quad (10)$$

where, C_0 is the highest initial dye concentration (mg L^{-1}). The value of R_L indicates, either the shape of adsorption isotherm is favourable ($0 < R_L < 1$) or unfavourable ($R_L > 1$) or linear ($R_L = 1$) or irreversible ($R_L = 0$).

To study the applicability of the Langmuir and Freundlich isotherms, the dye adsorption onto CF-g-PAM was done at initial dye (II) concentrations ranging from 50-300 mg L^{-1} using 30 mg copolymer as adsorbent, 20 mL contact volume, 4 h contact time, 150 rpm and pH 2 at two different temperatures (20 °C and 30 °C). Linear plots of C_e/q_e against C_e and $\log q_e$ versus $\log C_e$ are plotted respectively and the values of Q_{\max} , b , k_f , $1/n$, and R^2 (correlation coefficient values) of all isotherms models are shown in Table 4.

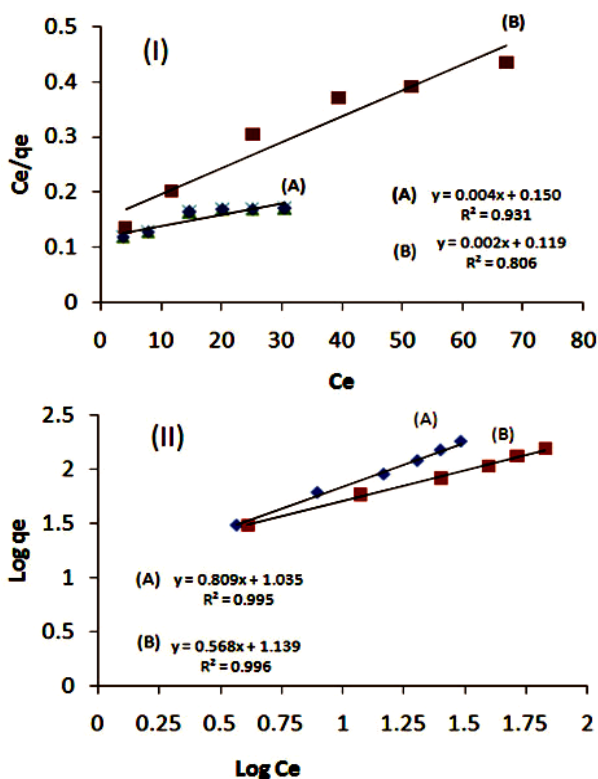


Fig. 10. (I) Langmuir adsorption isotherms (A) at 20 °C (A); (B) 30 °C; (II) Freundlich isotherms (A) 20 °C, (B) 30 °C.

The correlation coefficient values (R^2) showed that the adsorption equilibrium data better conformed to Freundlich isotherm model which indicate surface heterogeneity of the adsorbent and multilayer adsorption (Fig. 10). The higher value of $1/n$ (at 30 °C) showed the favourability and heterogeneity of adsorption.

Langmuir isotherm indicated high Q_0 (500 mg g^{-1} at 30 °C) for the adsorbent which indicated that the adsorbent has a significantly high capacity to remove dye (Table 5).

The values of Langmuir constant (b) at 20 °C and 30 °C were calculated to be 0.0266 and 0.0168 however the value of Q_0 and effect of temperature on dye uptake indicate the sorption process to be endothermic. This anomaly of results may be attributed to availability of heterogamous adsorption surface sites at the adsorbent c.f. adsorption equilibrium data better conformed to the Freundlich isotherm. Langmuir model fails to account for the surface roughness of the adsorbent and any possible adsorbate/adsorbate interactions. It appears that the temperature affects the dye-dye interaction at the adsorbate surface and hence the Q_0 [43]. The values of R_L showed that the adsorption is highly favourable.

Table 4. Langmuir and Freundlich constants.

Temperature (°C)	Q_{\max}	Langmuir isotherm			Freundlich isotherm			
		b (L mg^{-1})	R^2	R_L	bC_0	$1/n$	k_f	R^2
20	250	0.0266	0.931	0.2727	2.66	0.809	10.83	0.995
30	500	0.0168	0.806	0.3731	1.68	0.568	13.77	0.996

It is interesting to compare the sorption features of the RB_{H5G} dye between CF-g-PAM and various sorbents reported in the literature (Table 5).

Table 5. Some reported adsorbents for Reactive blue dyes.

Adsorbent	Dye	pH	Time (h)	Q_{\max} (mg/g)	Ref.
Chitosan-g-PMMA	RBH5G	7	3	178	[42]
Chitosan	RBH5G	7	3	92	[42]
Citrus waste biomasses	RB19	2	-	14.8	[44]
Citrus waste biomasses	RB29	2	-	27.4	[44]
Modified guar gum and silica based composite	RB4	--	1/3	579.01	[45]
CF-g-PAM	RB H5G	2	4	500	Present study

Desorption studies

CF-g-PAM was tested for its adsorption capacity in terms of its reusability for six consecutive cycles. A sorbent dose of 30 mg could almost completely adsorb 100 mg L^{-1} of dye solution. Almost complete (98.5 %) desorption of the loaded dye (in 2 h) could be achieved using 0.1 M NaOH in the 1st cycle. A loss of 1–2% of the dye was observed during stripping. In consecutive cycles, the adsorbent showed a steady decline in its performance, both in adsorption as well as desorption (Fig. 11). Though % removal decreased per cycle, the adsorbent was capable of eliminating the dye from the solution, proving the uninhibited efficiency of CF-g-PAM for a very long time.

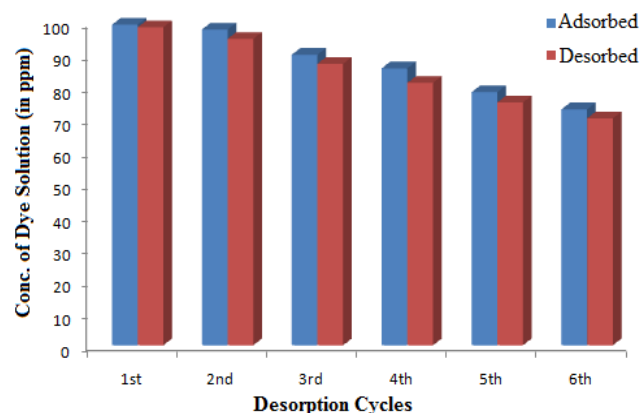


Fig. 11. Reusability of CF-g-PAM by adsorption-desorption process for six consecutive cycles.

Hence, it appeared that during desorption only the dye molecules which were electrostatically adsorbed were desorbed. It was likely that both electrostatic and complexation reaction occurred between the sorbent and the dye; therefore, complete desorption was not possible more so in the later cycles.

Conclusion

Ceric ammonium sulphate-sodium disulfite redox system has been successfully used to obtain exceptionally high % G and % E for grafting of poly(acrylamide) at *Cassia fistula* seed polysaccharide. The copolymer (CF-g-PAM) could effectively remove Reactive Blue (H5G) dye from synthetic dye solution. The adsorption equilibrium was quickly achieved in 4 h at an optimum pH 2. The equilibrium data fitted better to Freundlich isotherm indicating heterogeneous adsorbent sites at the copolymer. Langmuir isotherm indicated high monolayer adsorption capacity (Q_0) for the dye adsorption (500 mg/g) at 30 °C. The study can be extended to exploit CF-g-PAM for the removal and recovery of dyes from industrial textile effluent. This study can lead to a meaningful utilization of nonconventional seed gum from *Cassia fistula* for anionic azo dyes removal after its poly(acrylamide) modification.


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