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Adsorption of anionic dyes on chitosan grafted poly(alkyl methacrylate)s

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ABSTRACT

Chitosan grafted poly(alkyl methacrylate)s (namely chitosan grafted poly(methyl methacrylate) (ChgPMMA), chitosan grafted poly(ethyl methacrylate) (ChgPEMA), chitosan grafted poly(butyl methacrylate) (ChgPBMA) and chitosan grafted poly(hexyl methacrylate) (ChgPHMA)) were synthesized and characterized by using FT-IR and ^{13}C NMR techniques. The adsorption batch experiments on these grafted copolymers were conducted by using an anionic sulfonated dye, Orange-G. A pseudo-second-order kinetic model was used to determine the kinetics of adsorption. The effect of grafting, effect of process variables and the effect of different sulfonated anionic dyes (Orange-G, Congo Red, Remazol Brill Blue R and Methyl Blue) on the adsorption kinetics was determined. The Langmuir and Freundlich models were used to fit the adsorption isotherms and from the values of correlation coefficients (R^2), it was observed that the experimental data fits very well to the Langmuir model. The values of the maximum adsorption capacity of the adsorbents follow the order: ChgPMMA > ChgPEMA > ChgPBMA > ChgPHMA > chitosan.

1. Introduction

Dye effluents discharged from textile and paper/pulp industries are major sources of aquatic pollution. Several methods such as coagulation, biodegradation, adsorption, membrane separation, ion-exchange, incineration, etc. have been reported for waste water treatment. Among all these methods, adsorption is a both an effective and economical method for the removal of dyes from aqueous solutions [1,2]. Even though the adsorption of dyes on to activated carbon is effective, its widespread use has been limited because of high cost and problems with its disposal [2].

Adsorption in presence of different biosorbent materials such as agricultural wastes, bacterial biomass and biopolymers have been reported in literature [3]. In particular, chitosan has proved to be an effective biosorbent for removing the dyes from aqueous solutions because of its non-toxicity, biocompatibility, biodegradability, antibacterial property and high sorption capacity [4]. Chitosan and their derivatives have a high affinity for adsorption towards reactive and disperse dyes [5–7]. A detailed review on dye removal from aqueous solutions by adsorption using chitosan has been presented [1].

Chitosan is often grafted with polymers to improve its adsorption and mechanical properties. Jayakumar et al. have presented a detailed review on graft copolymerized chitosan and their applications [8]. Chitosan has been grafted with poly(acrylic acid) [9], poly(methacrylic acid) [10,11], poly(methyl methacrylate) [12] and modified with montmorillonite [13], β-cyclodextrin [14], fatty acid glycidyl [15], and crosslinked with glutaraldehyde [16]. All these materials have been successfully used for the adsorption of metal ions and dyes.

However, the effect of the alkyl group substituent of the grafted polymer on the adsorption kinetics has not been investigated. In the present study, a series of chitosan grafted poly(alkyl methacrylate)s has been synthesized and used for the adsorption of different types of sulfonated anionic dyes. The present study also determines the effect of process variables, grafting percentage and different dyes on the adsorption kinetics.

2. Experimental

2.1. Materials

Chitosan (molecular weight of 300 kDa and 81% of degree of deacetylation) was purchased from Sigma Aldrich (USA) and used without any further purification. All the monomers methyl methacrylate (MMA), ethyl methacrylate (EMA), n-butyl methacrylate (BMA) and hexyl methacrylate (HMA) were purchased from Sigma Aldrich (USA) and used after washing with 5% alkali solution to remove phenolic inhibitor. Potassium persulfate from S. D. Fine Chemicals (India) and ascorbic acid from Sisco research laboratories (India) were used without further purification. Acetone and formic acid (90%) were obtained from Merck (India). The dyes, Orange-G

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Table 1
Experimental details for the synthesis of chitosan grafted poly(alkyl methacrylate)s.

Experimental conditions for the synthesis of chitosan grafted poly(methyl methacrylate)				
Temperature: 45 °C Ascorbic acid = 0.49 g		Time: 2 h Potassium persulfate = 0.06 g		
ChgPMMA	Chitosan (g)	MMA (mL)	Grafted copolymer (g)	%*G*
A_1	0.2	3.2	0.5	150
A_2	0.225	2.9	0.6	167
A_3	0.25	2.65	0.74	196
A_4	0.275	2.4	0.95	210
Experimental conditions for the synthesis of chitosan grafted poly(ethyl methacrylate)				
Temperature: 50 °C Ascorbic acid = 0.57 g		Time: 6 h Potassium persulfate = 0.08 g		
ChgPEMA	Chitosan (g)	EMA (mL)	Grafted copolymer (g)	%*G*
B_1	0.2	3.5	0.66	229
B_2	0.25	3	0.61	144
B_3	0.275	2.75	0.81	195
B_4	0.3	2.5	0.69	130
Experimental conditions for the synthesis of chitosan grafted poly(butyl methacrylate)				
Temperature: 60 °C Ascorbic acid = 0.58 g		Time: 10 h Potassium persulfate = 0.1 g		
ChgPBMA	Chitosan (g)	BMA (mL)	Grafted copolymer (g)	%*G*
C_1	0.225	3.95	0.79	251
C_2	0.25	3.7	0.74	196
C_3	0.275	3.45	0.89	223
C_4	0.3	3.2	0.99	260
Experimental conditions for the synthesis of chitosan grafted poly(hexyl methacrylate)				
Temperature: 70 °C Ascorbic acid = 0.61 g		Time: 12 h Potassium persulfate = 0.12 g		
ChgPHMA	Chitosan (g)	HMA (mL)	Grafted copolymer (g)	%*G*
D_1	0.2	4.9	0.48	140
D_2	0.225	4.7	0.47	109
D_3	0.275	4.3	0.7	154
D_4	0.3	4	0.88	193

Note: 75 mL of 5% formic acid solution was used for all the experiments.

(OG), Congo Red (CR), Remazol Brill Blue R (RBBR) and Methyl Blue (MB) were purchased from S. D. Fine Chemicals (India). All dyes were at least 95% pure and the initial concentration reported in this study is after adjusting the concentration based on purity. Though all these are anionic sulfonated dyes, they belong to different structural groups: Orange-G is monoazo with $\lambda_{max} = 480$ nm, Congo Red is diazo with $\lambda_{max} = 500$ nm, Remazol Brill Blue R is anthraquinonic with $\lambda_{max} = 593$ nm and Methyl Blue is triaryl methane with λ_{max} at 600 nm.

2.2. Synthesis of chitosan grafted poly(alkyl methacrylate)s

Chitosan grafted poly(alkyl methacrylate)s namely chitosan grafted poly(methyl methacrylate) (ChgPMMA), chitosan grafted poly(ethyl methacrylate) (ChgPEMA), chitosan grafted poly(butyl methacrylate) (ChgPBMA) and chitosan grafted poly(hexyl methacrylate) (ChgPHMA) having different grafting percentages were synthesized by taking calculated amounts of chitosan, monomers (MMA, EMA, BMA and HMA), redox-initiator potassium persulfate/ascorbic acid at known temperature for desired time. The characteristics of redox-initiator are reported elsewhere [17] and the choice of temperature and time were taken from literature [12]. Calculated amount of chitosan was dissolved in 5% (v/v) formic acid aqueous solution and then calculated amounts of monomer and ascorbic acid were added to the mixture continuously stirring the mixture with a magnetic stirrer. The reaction mixture was kept in a thermostated water bath for 30 min followed by the addition of calculated amount of potassium persulfate. The final reaction mixture was poured in to a 100 mL standard flask and kept in a water bath maintained at desired reaction temperature. The reaction mixture was purged with N_2 gas prior to polymerization. The graft copolymerization was allowed for desired time and then the reaction mixture was precipitated by using acetone to separate chitosan grafted poly(alkyl methacrylate) from the homopolymer. The homopolymer dissolves in acetone and grafted copolymer is precipitated. The precipitated copolymer was then subjected to extraction with acetone using Soxhlet apparatus for 8 h to remove all the homopolymer. Similar methodology has been used for the synthesis of chitosan derivatives [12,18]. The exact details and amounts of reagents used for all the experiments are shown in Table 1.

The synthesized copolymers or adsorbents were dried at 50 °C to avoid any hydration (or solvation) of adsorbents. The gravimetric analysis has been effectively used to determine grafting percentage in previous studies [12,18,19] and the percentage of grafting (%*G*) was calculated gravimetrically, using the following equation.

$$\%G = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 and W_2 are the weights of the initial chitosan and grafted chitosan after extraction and drying. The general chemical structure of chitosan grafted poly(alkyl methacrylate)s is shown in Fig. 1.

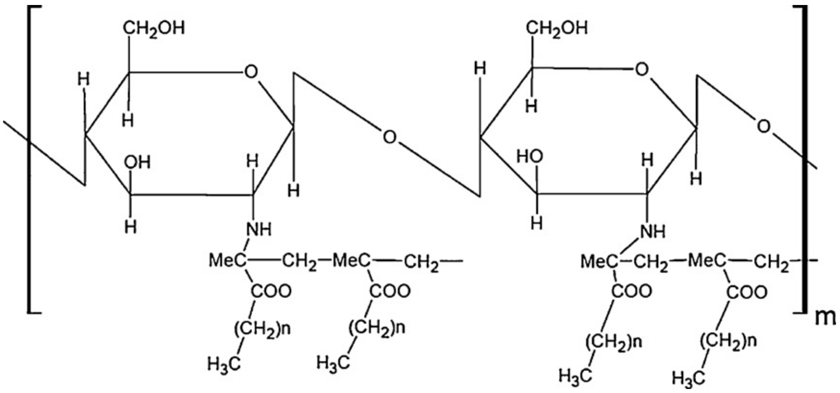

Fig. 1. The general structure of chitosan grafted poly(alkyl methacrylate)s. 'm' indicates the chain length of the chitosan grafted copolymer. $n = 0$ for ChgPMMA, $n = 1$ ChgPEMA, $n = 3$ for ChgPBMA and $n = 5$ for ChgPHMA.

2.3. Characterization of grafted chitosan

All the chitosan grafted poly(alkyl methacrylate)s were characterized by NMR and FT-IR.

2.3.1. Solid-state ^{13}C NMR characterization

Solid ^{13}C NMR characterization was carried out using 300 MHz, Bruker FT-NMR spectrometer using glycine as a reference substance for resonance frequency.

2.3.2. FT-IR characterization

Chitosan and chitosan grafted copolymer samples were mixed with KBr powder to make pellets for further analysis by FT-IR spectrometer. FT-IR spectra of the copolymer pellets were recorded by using Perkin-Elmer Spectrum RX-1 spectrometer in the transmission mode at a resolution of 4 cm^{-1} with the scanning range of 4400–450 cm^{-1}.

2.4. Adsorption batch experiments

Adsorption experiments were carried out by using all grafted samples (with different grafting percentages) as adsorbents. Adsorption experiments were carried out by using 50 mL of different dye solutions of different initial concentrations for different adsorbent dosages. For each experiment, 50 mL of dye stock solution along with the adsorbent were taken in a 100 mL beaker and stirred by using a magnetic stirrer for 6 h at a known temperature (maintained by using a feedback controller). The pH of the dye solution was adjusted to 7 for all the adsorption kinetic studies and equilibrium adsorption studies except for the study of the effect of pH, in which the pH was varied from 4 to 7 by using 0.1 M hydrochloric acid. The samples of the dye solution during the course of adsorption were collected at regular intervals of time and centrifuged to remove the adsorbent.

The absorption spectra of dye solutions before and after adsorption were recorded by using UV–vis spectrophotometer (Shimadzu-1700) in the range of 400–800 nm. The concentrations of dye solutions were determined at a wavelength ($\lambda_{\max}$) corresponding to the maximum absorbance, calibrated using Beer–Lambert's law.

3. Modeling

3.1. Adsorption kinetics

Kinetic analysis is required to obtain an insight of the rate of adsorption and the rate limiting step of the transport mechanism, which are primarily used in the modeling. To determine the kinetics of adsorption, a pseudo-second-order model was used [20]

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \qquad (2)$$

where k_s is the rate constant for pseudo-second-order adsorption (g mg^{-1} min^{-1}), c_0 is the initial dye concentration (mg L^{-1}), c_e is the equilibrium dye concentration (mg L^{-1}), V is the volume of dye solution used for adsorption (L), W is the weight of the adsorbent used (g), q_e is the amount of dye adsorbed (mg g^{-1}) at equilibrium and is defined as $(c_0 - c_e)V/W$. q_t is the amount of dye adsorbed at any time t. By solving the above Eq. (2) with the initial condition $q_t = 0$ at $t = 0$,

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e}t \qquad (3)$$

The values of the pseudo-second-order rate constant, k_s and the equilibrium dye uptake, q_e can be obtained from the slope and intercepts of the plot t/q_t with time, t. This pseudo-second-order rate model [20] was observed to be valid for all the adsorption experiments.

The approaching equilibrium factor (R_W), which represents the characteristics of kinetic curve of an adsorption system is given by [21]

$$R_W = \frac{1}{1 + k_s q_e t_{ref}} \qquad (4)$$

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 $0.1 < R_W < 0.01$; and it is drastically approaching equilibrium when $R_W < 0.01$.

3.2. Equilibrium isotherms

The relationship between adsorbed dye concentration and concentration of the solution at equilibrium is described by isotherm models, of which Langmuir and Freundlich are the most widely used equations [22].

Langmuir adsorption isotherm assumes monolayer adsorption of adsorbate over a homogeneous adsorbent surface with finite number of identical sites, which are energetically equivalent and negligible interaction between the adsorbed molecules. The Langmuir adsorption isotherm in the linear form is expressed as

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m K} \qquad (5)$$

where c_e is the equilibrium dye concentration (mg L^{-1}), q_e is the equilibrium amount of dye adsorbed per unit weight of adsorbent (mg g^{-1}), q_m is the maximum amount of dye adsorbed per unit weight of adsorbent to form a complete monolayer coverage ($\mathrm{mg\,g^{-1}}$) and K is the Langmuir adsorption constant ($\mathrm{L\,mg^{-1}}$).

The Freundlich adsorption isotherm assumes multilayer adsorption and it is applicable to adsorption on heterogeneous surfaces with interaction between the adsorbed molecules. The Freundlich isotherm is expressed as

$$q_e = K_f c_e^{1/n} \tag{6}$$

or

$$\ln q_e = \left(\frac{1}{n}\right) \ln c_e + \ln K_f \tag{7}$$

where K_f is the Freundlich adsorption constant which roughly indicates the adsorption capacity of the adsorbent and n is the Freundlich exponent which relates the adsorption intensity.

The affinity between the adsorbent and adsorbate can be calculated by substituting the value of Langmuir adsorption constant, K ($\mathrm{L\,mg^{-1}}$) in the expression for the dimensionless separation factor, R_L, which is given by [23]

$$R_L = \frac{1}{1 + Kc_0} \tag{8}$$

where c_0 is the highest initial dye concentration ($\mathrm{mg\,L^{-1}}$). The value of R_L indicates, either the shape of adsorption isotherm is favorable ($0 < R_L < 1$) or unfavorable ($R_L > 1$) or linear ($R_L = 1$) or irreversible ($R_L = 0$).

The favorable parameter (Kc_0) is given by

$$Kc_0 = \left(\frac{1}{R_L}\right) - 1 \tag{9}$$

The values of Kc_0 can be divided into five intervals and the shapes of the adsorption isotherms in these five intervals are quite different as described in literature [23]. When Kc_0 is zero, the isotherm is linear; when it varies from 1 to 10, it is termed as favorable and when its value is above 10, the isotherm is termed as highly favorable [23].

4. Results and discussion

4.1. Characterization of chitosan grafted poly(alkyl methacrylate)s

4.1.1. Solid-state ^{13}C NMR

Solid-state ^{13}C NMR spectroscopy was used to characterize the grafted copolymers (adsorbents). The solid-state ^{13}C NMR spectra of ChgPEMA and ChgPBMA are shown in Fig. 2. Due to the presence of poly(alkyl methacylate)s in the grafted copolymers, a peak corresponding to C=O carbon of alkyl methacrylate [21,24] at $\delta = 177$ is observed in all the adsorbents (grafted copolymers). The peaks at $\delta = 14.4$, 45.5, 56.5 and 60.9 in Fig. 2(a) represent triad distribution of α-$\mathrm{CH_3}$, quaternary, $-\mathrm{CH_2}$, $-\mathrm{OCH_2}$ carbons of PEMA grafts [21,25,26], confirming the grafting of poly(ethyl methacrylate) on to chitosan. The other peaks at $\delta = 71.3$, 75.1, 101 and 138 in Fig. 2(a) represent the presence of anomeric carbons, carbons linked to amino group and other carbons of polysaccharide [21]. Similarly, the peaks at $\delta = 14.2$ and 45.2 in Fig. 2(b) represent the triad distribution of α-$\mathrm{CH_3}$ and quaternary carbons of PBMA grafts [24]. The peaks at $\delta = 56.4$ and 65.2 corresponding to $-\mathrm{CH_2}$ grafts of PBMA and the peak at 70.7 corresponding to $-\mathrm{OCH_2}$ group of PBMA [19] can be identified in Fig. 2(b), confirming the grafting of poly(butyl methacrylate) on to chitosan. The other peaks at $\delta = 75.4$, 97 and 137 show the existence of anomeric carbons, carbons attached to amino group and other carbons of polysaccharide. Similar spectra were observed for ChgPMMA and ChgPHMA (see supplementary information, Fig. S2(c) and S2(d)).

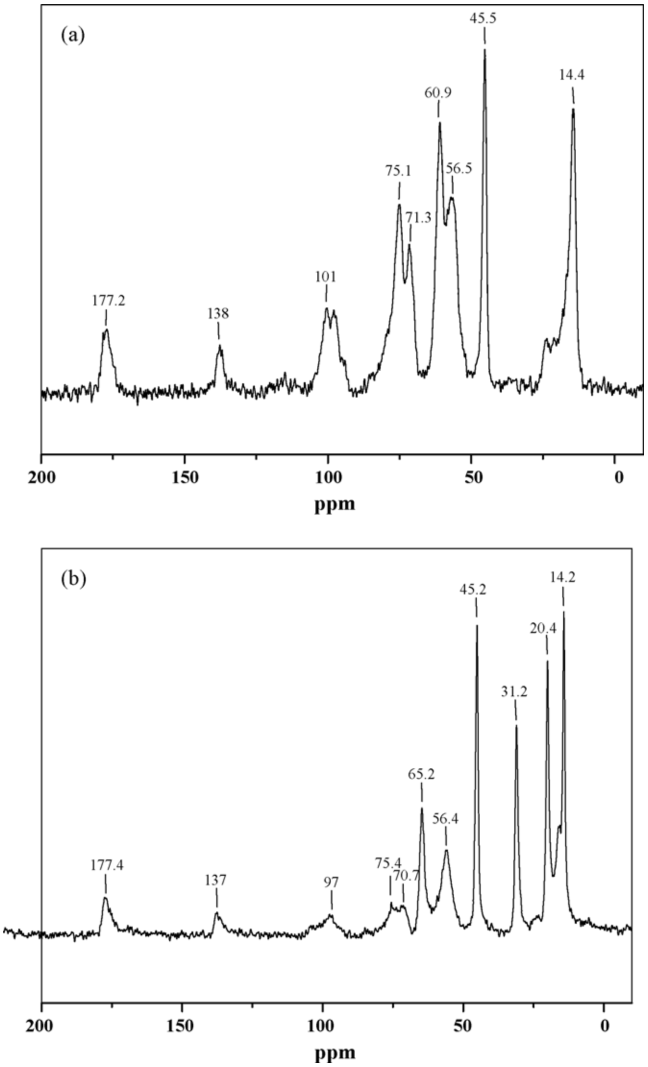

Fig. 2. Solid-state ^{13}C NMR spectra of (a) chitosan grafted poly(ethyl methacrylate) and (b) chitosan grafted poly(butyl methacrylate).

4.1.2. FT-IR characterization

The FT-IR spectra of chitosan and ChgPMMA are shown in Fig. 3(a) and (b), respectively. The FT-IR spectra of all the other grafted copolymers are shown in Fig. S3(c), S3(d) and S3(e) (see supplementary information), respectively. The FT-IR spectrum of chitosan shows some characteristic absorption bands at 3437 $\mathrm{cm^{-1}}$ corresponding to the stretching vibration of O–H, extension vibration of N–H and intermolecular hydrogen bonds of polysaccharide moieties, at 1639 $\mathrm{cm^{-1}}$ due to N–H bending vibrations indicating the presence of $\mathrm{NH_2}$ group on C2 of the glucosamine unit and at 1083 $\mathrm{cm^{-1}}$ corresponding to stretching vibrations of –C–O–C bond [25].

In all the grafted polymers, a broad peak around 3431 $\mathrm{cm^{-1}}$ due to stretching vibrations of N–H and O–H bonds and a peak around 1639 $\mathrm{cm^{-1}}$ (N–H bending vibrations) are observed, which indicate the existence of the chitosan moiety in the grafted copolymers. A sharp peak is observed around 1735 $\mathrm{cm^{-1}}$ for the grafted samples corresponding to ester carbonyl stretching vibrations of poly(alkyl methacrylate)s. The vibration peaks corresponding to the out-of-plane C–H bending, rocking of $\mathrm{CH_2}$ and the stretching vibration of C–N we observed at frequencies 646, 756 and 852 $\mathrm{cm^{-1}}$, respectively, in all the grafted polymers. The –O–C–C stretching [25] in grafted copolymers is characterized by the presence of a peak around 1094 $\mathrm{cm^{-1}}$.

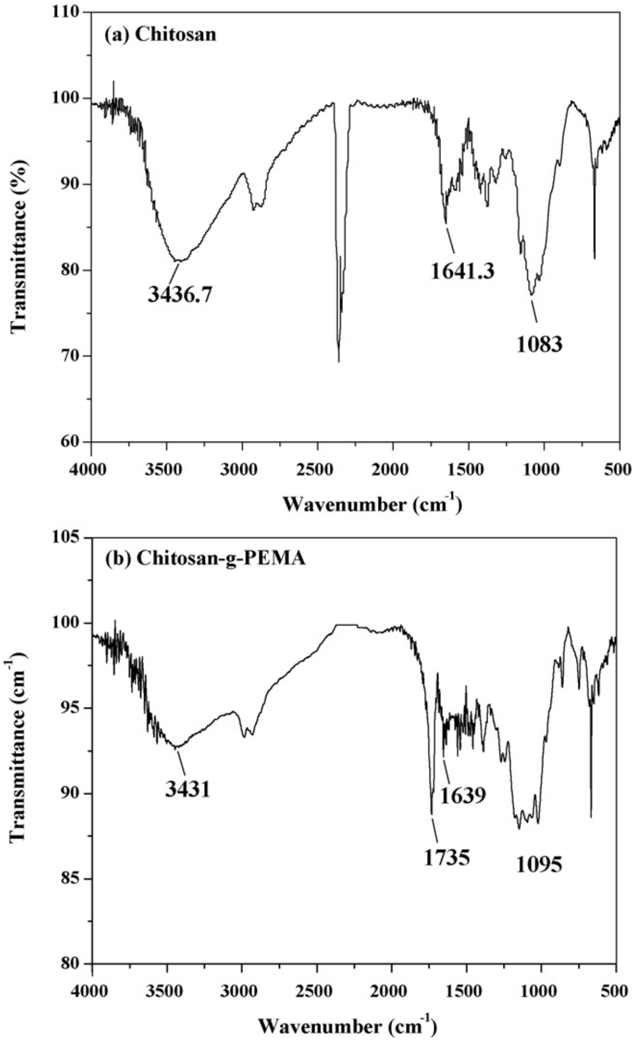

Fig. 3. FT-IR spectra of chitosan and chitosan grafted copolymers: (a) chitosan and (b) ChgPMMA.

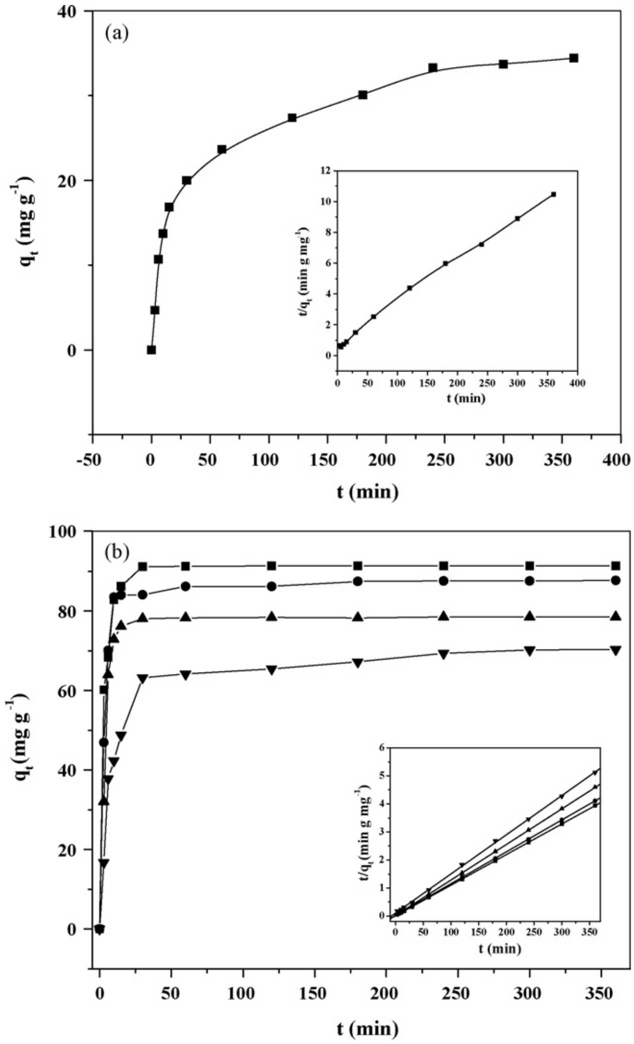

Fig. 4. Variation of dye uptake with time at pH = 7 for (a) chitosan and (b) ChgPEMA copolymers (■) %*G*-229, (●) %*G*-195, (▲) %*G*-144 and (▼) %*G*-130. The inset shows the pseudo-second-order model for the adsorption data.

This characterization clearly shows that chitosan has been successfully grafted on the polymers.

4.2. Kinetics and equilibrium of adsorption

The experimental data was fitted with linearized forms of pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion model equations [22]. The result of the regression analysis showed that adsorption on chitosan was best described by the pseudo-second-order equation, which showed higher correlation coefficients. The equilibrium capacities calculated from pseudo-second-order model agreed closely with the capacities found from isotherm studies. Further, several other investigations determining the kinetics of adsorption onto chitosan have also reported better correlations for the pseudo-second order model compared to other models [22]. Therefore, the kinetics was modeled using the equation for the pseudo-second-order model, given by Eq. (3).

4.2.1. Effect of grafting

To investigate the effect of grafting on the adsorption of dyes, experiments were conducted for adsorption at pH of 7 from 50 mL of 300 ppm OG with 150 mg of chitosan and grafted polymers having different grafting percentages. The results are shown in Fig. 4(a) and (b) for the adsorption on chitosan and ChgPEMA while Fig. 4(c), (d) and (e) (see supplementary information) show the results for the adsorption on ChgPMMA, ChgPBMA and ChgPHMA, respectively. The inset of Fig. 4 shows linear plots and thus the validation of pseudo-second-order model for the sorption data.

The values of q_e (amount of dye adsorbed at equilibrium) and k_s (rate constant for the pseudo-second-order adsorption) for the adsorption of OG on ungrafted chitosan are 34 mg g^{-1} and 1.32×10^{-4} g mg^{-1} min^{-1} (Table 2). The values of q_e, k_s (determined from Eq. (3)) and the R_W (determined by Eq. (4)) of all the grafted polymers are shown in Table 2. It is clear that the grafted polymer exhibit much higher adsorption capacity compared to that of chitosan. The values of R_W indicate that the characteristic adsorption curve is drastically approaching equilibrium for most of the cases.

It is clearly evident from Fig. 4(b) that the percentage of adsorption increases with an increase in grafting percentage for ChgPEMA. For example, the adsorption of the dye on ChgPEMA increases from 72.2 to 91.4 mg g^{-1} as the %grafting increases from 130 to 220. This is because of the increase in poly(ethyl methacrylate) grafts, which are responsible for the enhancement in the adsorption of dyes. Similar results were observed for the other grafted copolymers, ChgPMMA, ChgPBMA and ChgPHMA. These results are shown in Fig. S4(c), 4(d) and 4(e), respectively (see supplementary information).

Table 2
Pseudo-second-order sorption kinetics of Orange-G on chitosan grafted poly(alkyl methacrylate)s: 300 ppm dye solution (50 mL) and 150 mg of adsorbent for all the experiments.

%*G*	q_e (mg g^{-1})	$k_s \times 10^2$ (g mg^{-1} min^{-1})	R_W
ChgPMMA			
245	94	5	0.0011
196	87.2	1.3	0.0044
166	83.3	1.2	0.0050
150	80.1	0.7	0.0088
ChgPEMA			
229	91.4	1.2	0.0045
195	86.7	0.8	0.0072
144	78.3	0.9	0.0070
130	72.2	0.17	0.0391
ChgPBMA			
260	88.5	1.3	0.0043
251	86.9	1.6	0.0036
223	85.5	1.5	0.0039
196	84	1.4	0.0042
ChgPHMA			
193	80.6	7.7	0.0008
154	77.5	1.3	0.0049
140	75.7	1.6	0.0041
109	71.4	0.8	0.0087
Ungrafted chitosan			
0	34	0.013	0.5308

4.2.2. *Initial dye concentration*

Fig. 5 shows the effect of initial dye concentration on the adsorption kinetics of the ChgPEMA of %*G* 130. The inset of Fig. 5 shows the pseudo-second-order model for the sorption data. The initial pH of the dye solution was adjusted to 7. The values of q_e (obtained from the slopes of pseudo-second-order model) for the adsorption of 100, 200, 300 and 500 ppm Orange-G dye solutions (50 mL) using ChgPEMA of %*G* 130 (150 mg of adsorbent) are 30.3, 58.8, 72.2 and 88.9 mg g^{-1}, respectively. Similar profiles were observed for all other grafted copolymers. From Fig. 5, it is clear that the adsorption capacity increases with increase in initial dye concentration (100–500 ppm), since the driving force (to overcome liquid and solid phase mass transfer resistances) for the adsorption process increases with increasing the dye concentration.

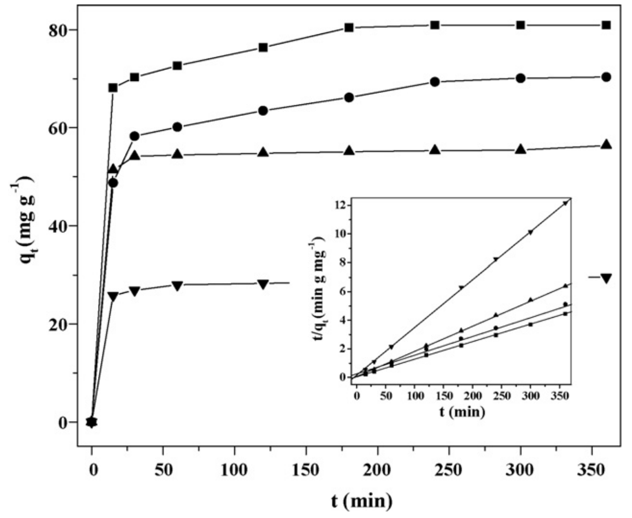

Fig. 5. Variation of dye uptake with time for ChgPEMA of 130%*G* (150 mg) for different initial dye (Orange-G) concentrations at pH = 7: (■) 500 ppm, (●) 300 ppm, (▲) 200 ppm and (▼) 100 ppm. The inset shows the pseudo-second-order model for the adsorption data.

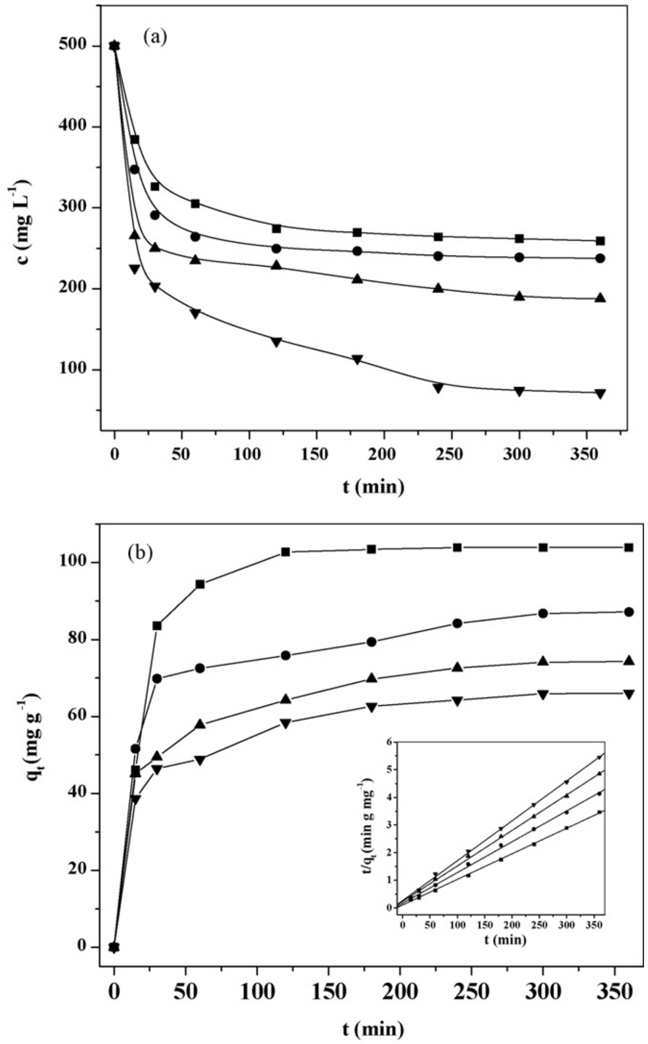

Fig. 6. (a) Variation of concentration with time and (b) variation of dye uptake with time for ChgPEMA of 130%*G* for the adsorption of Orange-G solution of concentration 500 ppm for different dosages of adsorbent at pH = 7: (■) 125 mg, (●) 150 mg, (▲) 200 mg and (▼) 300 mg. The inset of (b) shows the pseudo-second-order model for the adsorption data.

4.2.3. *Adsorbent dosage*

The effect of adsorbent amount (dosage) on the adsorption was investigated for the adsorption of Orange-G dye solution (50 mL) of initial concentration 500 ppm at pH of 7 using ChgPEMA of %*G* 130 as adsorbent. The variation of dye concentration with time is shown in Fig. 6(a). Fig. 6(b) shows the variation of q_t with time. The inset of Fig. 6(b) shows the pseudo-second-order model for the sorption data. The percentage removal of dye increased with increasing the adsorbent amount, as evident from Fig. 6(a). This is due to increase in adsorbent sites for the adsorption of dye with increased adsorbent dosage. The values of q_e, obtained from the model are 105.2, 88.9, 77.3 and 68.4 mg g^{-1} for 125, 150, 200 and 300 mg of adsorbent dosages, respectively. Even though the percentage of dye removal increased with adsorbent dosage, the adsorption capacity (mg of dye adsorbed/g of adsorbent) increased with decrease in adsorbent dosage. This is because the amount of dye in contact with unit weight of adsorbent increases with decrease in adsorbent dosage [8,26].

4.2.4. *Effect of pH*

pH plays an important role for the adsorption of dyes on chitosan grafted polymers. The adsorption capacity of anionic dyes on to chitosan derivatives strongly depends on surface charge, which eventually depends on the pH of the system. Zeta (ζ)-potential analysis indicated that the chitosan grafted PMMA particles in acetic solution were positively charged and have a ζ-potential of about 42 mV in acidic solution. Further, ζ-potential as a function of pH shows that this material has an isoelectric point [28] of pH 8.2. The reason for the adsorption of anionic dyes on to chitosan grafted polymers is mainly due to the protonation of polymer (poly(alkyl methacrylate)) grafts and ungrafted amine groups. The effect of pH for the adsorption of OG on ChgPEMA (%*G* 130) is shown in Fig. 7. In the present study, we observed that the dye uptake for OG adsorption is very high at low pH (acidic). The values of q_e, obtained from the model are 88.2, 82.5, 79.7 and 72.2 mg g^{-1} at pH values 4, 5, 6 and 7, respectively. The effect of pH for the adsorption of MB, RBBR and CR is similar as that of OG. The optimum pH operating range for the adsorption of dyes OG, MB, RBBR and CR is 3–6. Similar results have been reported in literature [27].

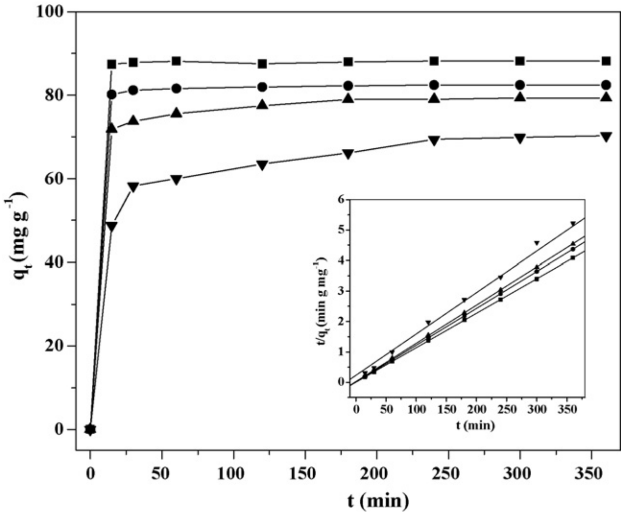

Fig. 7. Variation of dye uptake with time for ChgPEMA of 130%*G* for the adsorption of Orange-G solution of concentration 300 ppm at different pH values: (■) pH = 4, (●) pH = 5, (▲) pH = 6 and (▼) pH = 7. The inset shows the pseudo-second-order model for the adsorption data.

4.2.5. *Effect of different dyes*

The adsorption of four different anionic dyes OG, CR, RBBR and MB at pH = 7 on ChgPBMA with 260% grafting was studied. Fig. 8 shows the variation of amount of dye adsorbed per unit weight of adsorbent q_t, with time *t*, for these four different dyes. Fig. 8 shows that the adsorption capacity of these dyes on ChgPBMA follows the order RBBR > MB > CR > OG. The inset of Fig. 8 shows the pseudo-second-order model applied to the adsorption data of these dyes. The values of q_e (equilibrium amount of dye adsorbed) obtained from the pseudo-second-order model (Table 3) are 99.5, 98.5, 96.7 and 88.5 mg g^{-1} for the adsorption of RBBR, MB, CR and OG, respectively, which confirms the observed order of adsorption capacity for these dyes.

Table 3
The values of kinetic parameters at different experimental conditions and for different dyes.

Effect of initial dye concentration

Amount of adsorbent (ChgPEMA %*G*-130) = 150 mg

Dye (Orange-G) concentration (mg L^{-1})	q_e (mg g^{-1})	$k_s \times 10^2$ (g mg^{-1} min^{-1})	R_W
100	30.3	0.96	0.0169
200	58.8	0.69	0.0122
300	72.2	0.17	0.0391
500	88.9	0.10	0.0532

Effect of adsorbent (ChgPEMA %*G*-130) dosage

Dye (Orange-G) concentration = 500 mg L^{-1}

Amount of adsorbent (mg)	q_e (mg g^{-1})	$k_s \times 10^2$ (g mg^{-1} min^{-1})	R_W
125	105.2	0.11	0.0414
150	88.9	0.10	0.0532
200	77.3	0.09	0.0071
300	68.4	0.08	0.0089

Effect of pH

Dye (Orange-G) concentration = 300 mg L^{-1}
Amount of adsorbent (ChgPEMA %*G*-130) = 150 mg

pH	q_e (mg g^{-1})	$k_s \times 10^2$ (g mg^{-1} min^{-1})	R_W
4	88.2	4.35	0.0013
5	82.5	2.44	0.0025
6	79.7	0.57	0.0109
7	72.2	0.17	0.0391

Effect of different dyes

Amount of adsorbent (ChgPBMA %*G*-260) = 150 mg
Dye concentration = 300 mg L^{-1}

Dye	q_e (mg g^{-1})	$k_s \times 10^2$ (g mg^{-1} min^{-1})	R_W
RBBR	99.5	2.37	0.0021
MB	98.5	0.63	0.0080
CR	96.7	0.25	0.0203
OG	88.5	1.34	0.0042

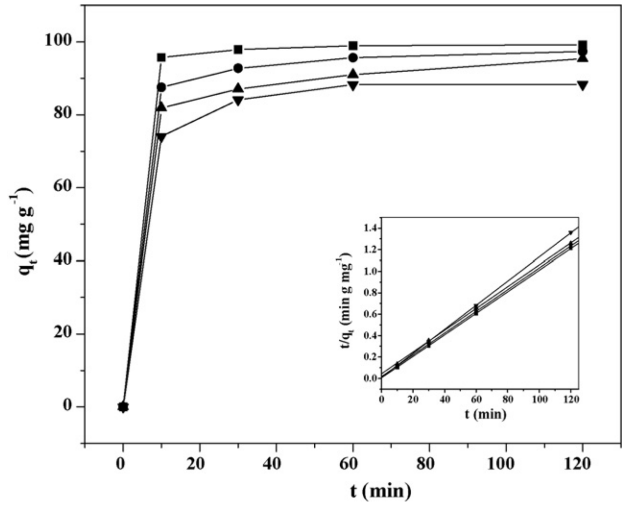

Fig. 8. Variation of dye uptake with time for ChgPBMA of 260%G (150 mg) for the adsorption of different sulfonated anionic dyes at 300 ppm at pH = 7: (■) Remazol Brill Blue R, (●) Methyl Blue, (▲) Congo Red and (▼) Orange-G. The inset shows the pseudo-second-order model for the adsorption data.

The observed differences in the adsorption capacities of these dyes may be due to the combined effect of pH of the solution, canonical resonances in the dye molecules due to the presence of amino groups, type of the dye and size of the dye molecules [29]. Further investigations are needed to understand the reason for such behavior and better design of adsorbents.

The values of kinetic parameters for the adsorption process at different experimental conditions and for different dyes correlated by using the pseudo-second-order model are summarized in Table 3.

4.2.6. Adsorption isotherms

The adsorption isotherms for the adsorption of Orange-G dye at pH = 7 using four different adsorbents ChgPMMA, ChgPEMA, ChgPBMA, ChgPHMA (approximately at the same percentage of grafting of 196%G) and chitosan were determined. The adsorption curves were modeled by using both Langmuir and Freundlich adsorption isotherms.

The Langmuir and Freundlich adsorption parameters are determined by plotting the experimental data based on Eqs. (5) and (7), respectively. The parameters that were determined and their corresponding correlation coefficients are listed in Table 4a. From the values of the correlation coefficient (R^2), it is clear that the adsorption curves fit very well to the Langmuir isotherm than Freundlich isotherm, indicating that the adsorption is monolayer coverage and the interaction between the adsorbed dye molecules is negligible.

The Langmuir adsorption isotherms for the adsorption of Orange-G dye on chitosan and ChgPEMA are shown in Fig. 9(a) and (b), respectively. The isotherms for the other grafted copolymers ChgPMMA, ChgPBMA and ChgPHMA (approximately at same percentage of grafting, i.e. 196%G) are shown in Fig. S9(c) to S9(e) (see supplementary information). From the values of the maximum adsorption capacity q_m (mg of dye/g of adsorbent) obtained from Langmuir adsorption isotherm, the adsorption capacity chitosan grafted poly(alkyl methacrylate)s follows the order: ChgPMMA > ChgPEMA > ChgPBMA > ChgPHMA. Further, these values of the maximum adsorption capacity q_m are much higher for the grafted polymers than that of chitosan (Table 4a). For example, the values of q_m are 4.5 times and 3.7 times higher for ChgPMMA and ChgPEMA, respectively, when compared to that of chitosan. The observed order of the adsorption capacity can be attributed to increase in steric hindrance, distortion of geometry and decrease in inductive effect with increase in number of carbon atoms of the alkyl group substituent.

Table 4a
Langmuir and Freundlich adsorption isotherm parameters for the four different copolymers for the adsorption of OG at the same 196%G.

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_m (mg g^{-1})	K (L mg^{-1})	R^2	K_f	N	R^2
ChgPMMA	435	0.016	0.993	21	2.08	0.976
ChgPEMA	360	0.013	0.996	12	1.99	0.971
ChgPBMA	290	0.011	0.998	11	1.97	0.957
ChgPHMA	265	0.010	0.997	10	2.04	0.95
Chitosan (ungrafted)	95	0.002	0.996	4	1.89	0.953

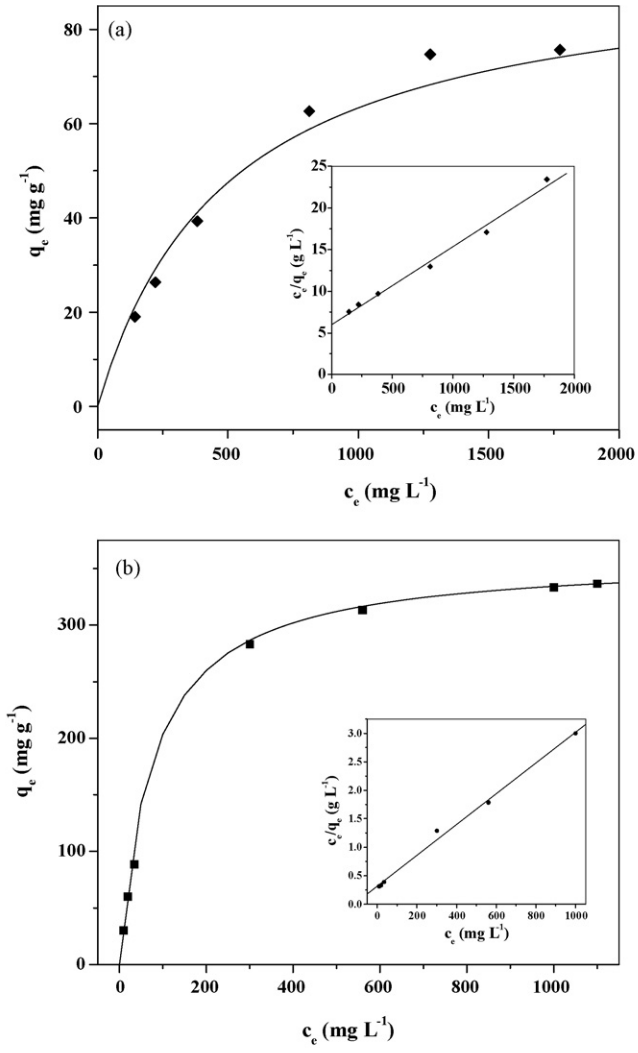

Fig. 9. Variation of equilibrium amount of dye adsorbed, q_e (mg g^{-1}) with equilibrium dye concentration, c_e (mg L^{-1}) for (a) chitosan and (b) ChgPEMA (%G-194). Insets show the linearized Langmuir adsorption isotherms for the corresponding adsorption curves.

The values of R_L (Eq. (8)) and Kc_0 for the adsorption of Orange-G dye using four different grafted copolymers (ChgPMMA, ChgPEMA, ChgPBMA and ChgPHMA approximately at same percentage of grafting, i.e. 196%G) and chitosan are shown in Table 4b. The value of R_L lies in between 0 and 1 and the value of Kc_0 is higher than 10 for all the four chitosan grafted polymers, indicating that the adsorption is highly favorable, based on the classification in the literature [23]. Even for the case of adsorption on chitosan, the value of Kc_0 is more than unity indicating that the isotherm is favorable. Similar results were observed for the adsorption of water soluble

Table 4b
The values of separation factor (R_L) and favorable parameter (Kc_0) for the adsorption of Orange-G on four different copolymers at the same 196%*G*.

Adsorbent	Kc_0	R_L
ChgPMMA	32	0.030
ChgPEMA	26	0.037
ChgPBMA	22	0.043
ChgPHMA	20	0.048
Chitosan	4	0.200

cationic dyes, methylene blue and malachite green using chitosan grafted poly(methacrylic acid) [15].

4.2.7. Adsorption mechanism

Sulfonated anionic dyes are electrostatically attracted by protonated amine groups of the chitosan and thus the dye adsorption is maximum in chitosan at pH of 4. However, at neutral pH, the amino group in chitosan is deprotonated and thus adsorption decreases [12]. The grafted copolymers, on the other hand, show high adsorption of the dyes even at neutral pH. This is because the ester groups at the grafted chitosan are primarily responsible for the adsorption. The maximum binding takes place at the copolymer grafts and only a negligible amount of NH_2 is available for binding after grafting [12]. Though some physical adsorption can occur at low dye concentration, the adsorption mechanism is primarily by chemisorption. The adsorption capacity of ChgPMMA is higher than ChgPHMA and the decrease in adsorption capacity with an increase in number of carbon atoms of the alkyl group substituent and be attributed to increase in steric hindrance and distortion of geometry.

5. Conclusions

A series of chitosan grafted poly(alkyl methacrylate)s was synthesized, characterized and used successfully for the adsorption of various sulfonated anionic dyes. The effect of various parameters such as grafting percentage, pH, dye concentration, adsorbent dosage on the adsorption was studied. The ability of the grafted polymers to adsorb different sulfonated anionic dyes was also determined. A pseudo-second-order model was used to study the adsorption kinetics and the experimental data was correlated by this model. The kinetic parameters indicated that the adsorption capacity follows the order RBBR > MB > CR > OG. The adsorption isotherms for the sorption of the dye on chitosan and the grafted polymers were determined and modeled using the Langmuir equation. The adsorption capacity follows the order: ChgPMMA > ChgPEMA > ChgPBMA > ChgPHMA > chitosan, with the adsorption equilibrium capacity of ChgPMMA being 4.5 times that of chitosan.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.01.003.

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