



Removal of Reactive Black 5 from aqueous solutions using magnetic chitosan resins

Khalid Z. Elwakeel*

Egyptian Water and Wastewater Regulatory Agency, Masraweya District, 5th Community, New Cairo city, Egypt

ARTICLE INFO

Article history:

Received 20 June 2008
Received in revised form
29 December 2008
Accepted 6 January 2009
Available online 23 January 2009

Keywords:

Chitosan
Magnetic
Reactive Black 5
Quaternary amine

ABSTRACT

Chitosan was cross-linked using glutaraldehyde in the presence of magnetite. The resin obtained was chemically modified through the reaction with tetraethylenepentamine followed by glycidyl trimethylammonium chloride, to produce chitosan/amino resin (R1) and chitosan bearing both amine and quaternary ammonium chloride moieties (R2), respectively. The uptake of Reactive Black 5 (RB5) from aqueous solutions using R1 and R2 resins was studied using batch and column methods. The resins showed high affinity for the adsorption of RB5 where an uptake value of 0.63 and 0.78 mmol/g was reported for resins R1 and R2, respectively at 25 °C. Both kinetics and thermodynamic parameters of the process were estimated. These data indicated an endothermic spontaneous adsorption process and kinetically followed the pseudo-second order model. Breakthrough and regeneration curves for the removal of RB5 were studied. The adsorbed dye was eluted from the investigated resins effectively.

Published by Elsevier B.V.

1. Introduction

Color effluents have been produced ever since the dyeing technique was invented. Various kinds of synthetic dyestuffs appear in the effluents of wastewater in various industries such as dyestuff, textiles, leather, paper . . . etc. It is recognized that public perception of water quality is greatly influenced by the color. Color is the first contaminant to be recognized in wastewater [1]. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable [2]. Over 100,000 commercially available dyes exist and more than 7×10^5 tonnes per year are produced annually [3,4]. Reactive dyes are the most common dyes used due to their advantages, such as bright colors, excellent colorfastness and ease of application [5,6]. Due to their good solubility, reactive dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. An indication of the scale of the problem is given by the fact that two percent of dyes that are produced are discharged directly in aqueous effluent [2,3]. Conventional methods for the removal of dyes in effluents include physical, chemical, and biological processes [7]. Unfortunately, reactive dyes are resistant to bacterial activity and biological treatment alone will take a long time to be effective [8]. Furthermore, it is difficult to remove reactive dyes using chemical coagulation due to the dye's high solubility in water [9]. Therefore, alternative technology must be developed to solve this problem. The use of adsorption

techniques for color removal from wastewater has already received considerable attention and several adsorbents have been developed for this purpose [10–14]. Adsorption onto activated carbon appears to be the best prospect of eliminating this dye. In spite of its good efficiency, this adsorbent is expensive and difficult to regenerate after use. Therefore, many researches in recent years have focused on the use of various low-cost adsorbents instead of activated carbon [15]. Recently, chitosan, a biopolymer of glucosamine, has exhibited a higher capacity for adsorption of colorant than activated carbon. In addition, chitosan is economically attractive, since it can be obtained from the deacetylation of chitin, and chitin is the second most abundant biopolymer in nature, next to cellulose [16]. Chelating resins and chelating magnetic resins represent an important category of promising adsorbents. They are highly selective, efficient and easily regenerable relative to other adsorbent materials [17]. Recently, the use of chelating and chelating magnetic resins for the removal of some dyes from aqueous solutions was reported by many authors [18–20]. The ultimate goal of this study is to develop new magnetic resins based on chitosan for the removal of Reactive Black 5 (RB5) from aqueous solutions. The factors affecting the removal behaviour will be studied. Thermodynamic as well as kinetic properties of the removal process will also be clarified.

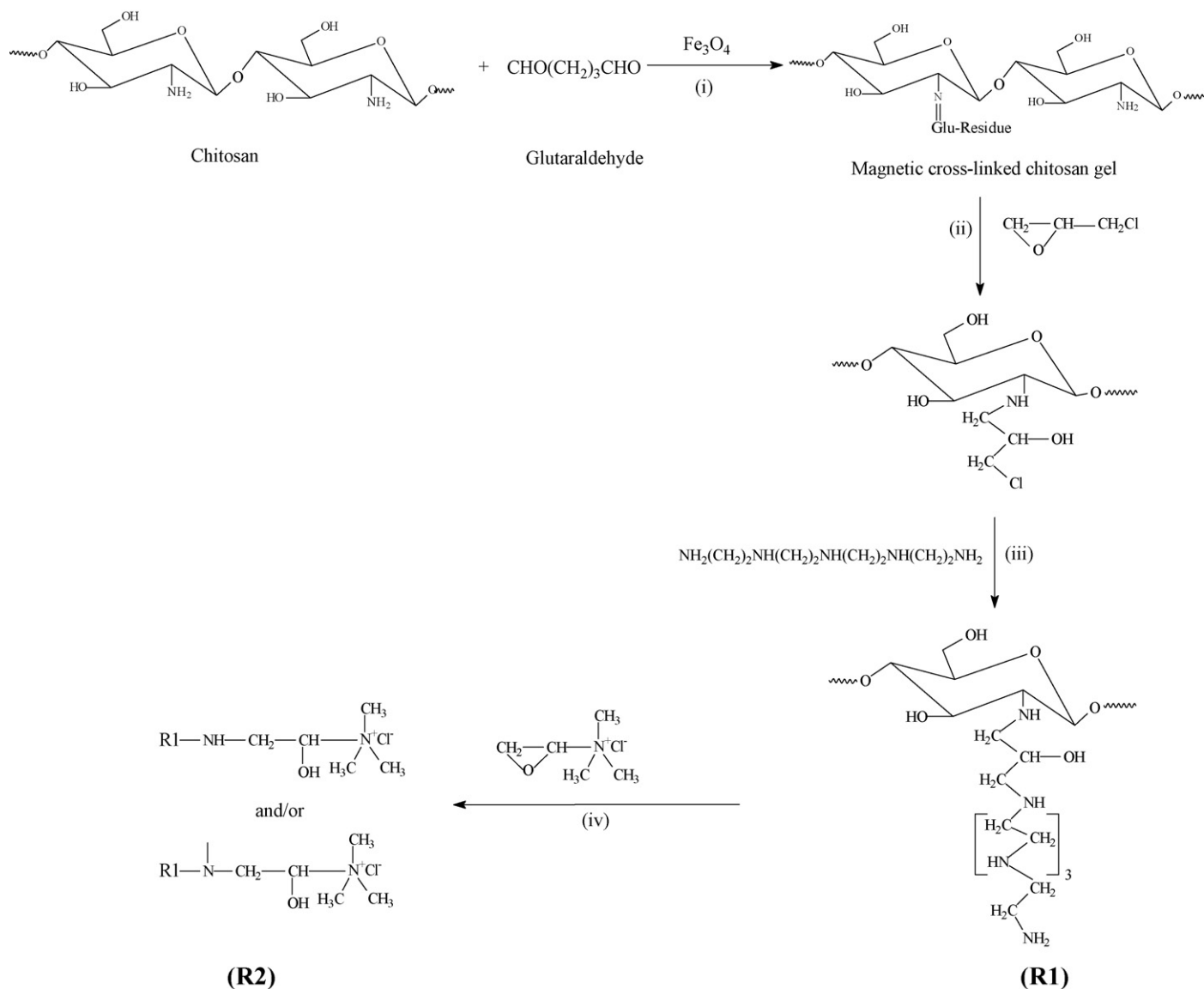
2. Experimental

2.1. Chemicals

Chitosan with degree of deacetylation (DD) of 82.1%, glutaraldehyde, tetraethylenepentamine (TEPA), glycidyl trimethylammonium chloride (GTMAC) and Reactive Black 5 (RB5) were Aldrich

* Tel.: +20 161694332.

E-mail addresses: Khalid.Elwakeel@yahoo.com, Khalid.Elwakeel@hotmail.com.



Scheme 1.

products. All other chemicals were Prolabo products and were used as received. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were used for preparing magnetite particles as reported earlier using modified Massart method [21,22].

2.2. Preparation of modified magnetic chitosan resins

The process of preparation takes place through subsequent steps (Scheme 1).

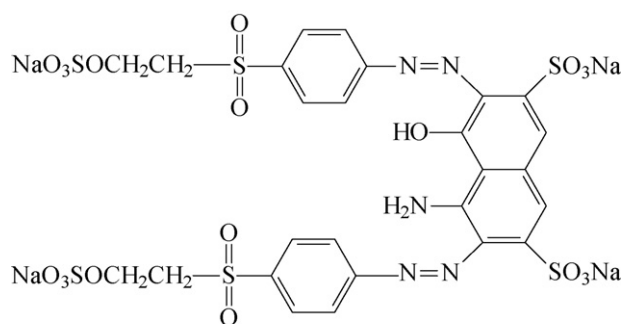
2.2.1. Preparation of the magnetic chitosan gel

Three grams of chitosan was dissolved in 20% aqueous solution of acetic acid. One gram of magnetite was added to chitosan solution and stirred until the solution became homogenous. Then 1 mL of glutaraldehyde solution was added and the solution was stirred with heating until gelatinous product was obtained. The gel obtained was washed with distilled water several times and kept for use.

2.2.2. Reaction with epichlorohydrine

The cross-linked chitosan gel obtained in the above step (i) was suspended in 70 mL isopropyl alcohol. Then 7 mL epichlorohydrine

(62.5 mmol) dissolved in 100 mL acetone/water mixture (1:1, v/v) was added. The above mixture was stirred for 24 h at 60 °C. The solid product obtained was filtered off and washed several times with water followed by ethanol.



Reactive Black 5

Scheme 2.

2.2.3. Reaction with tetraethylenepentamine (TEPA)

The product obtained in the step (ii) was suspended in 100 mL ethanol/water mixture (1:1, v/v) and then treated with 5 mL TEPA. The reaction mixture was stirred at 60 °C for 12 h. The product obtained was washed with water followed by ethanol. The produced chitosan/pentamine resin was dried in air and referred by (R1). The amine content in R1 was estimated using volumetric method of HCl according the early reported method [23,24] and was found to be 4.9 mmol/g.

2.2.4. Reaction with glycidyl trimethylammonium chloride (GTMAC)

The chitosan/pentamine product obtained in the step (iii) was suspended in 50 mL of water and treated with GTMAC. The reaction mixture was stirred at 60 °C for 24 h. The product was filtered and washed with distilled water, methanol, and acetone then dried in air and referred by (R2).

The concentration of quaternary amine groups on the modified chitosan resin (R2) was estimated by conductometric titration [25] using Hanna conductivity meter model EC215. A 0.1 g of resin was suspended in 200 mL of distilled water. Standard silver nitrate solution (0.01 M) was added dropwise to the suspension of the resin with continuous stirring and the conductivity was recorded. The end point was obtained from plotting the conductivity of a suspension of R2 against mL added of 0.01 M AgNO₃ (conductometric titration curve). The end point was detected at 35 mL AgNO₃. The concentration of quaternary ammonium sites (mmol/g) was calculated from equation

concentration of quaternary ammonium sites (mmol/g)

$$= \frac{M \times V}{W} \quad (1)$$

where M and V are the molarity (mol/L) and the volume (mL) of the titrant, respectively, and W is the weight of the resin. The concentration of quaternary ammonium groups was found 3.5 mmol/g resin.

2.3. Characterization of the resins

2.3.1. FT-IR analysis

Infra red spectra were performed using Nicolet IR200 FT-IR Spectrometer.

2.3.2. Water regain

Water regain factor, $W\%$, represents the percentage of water held intrinsically by the resin. For water regain determination, resin samples were centrifuged for 30 min at 1000 rpm to remove excess water and then weighed. These samples were then dried at 50–60 °C until complete dryness then weighed again. To calculate this factor, the following equation was applied:

$$W\% = \frac{100(W_w - W_d)}{W_w} \quad (2)$$

where W_w and W_d are weights (g) of the wet and dried resin respectively. Water regain values are (52 ± 3%) and (58 ± 3%) for R1 and R2 respectively, with insignificant differences when changing conditions. This value reflects the hydrophilic character of the resin type.

2.3.3. Surface area

The surface area of the prepared resins was measured by methylene blue adsorption as this material is known to be adsorbed as a monolayer only on solid sorbents. A standard solution of this material was prepared (0.02 g/L). A calibration curve for methylene blue was drawn ($\lambda = 660$ nm) by measuring diluents from standard stock. To calculate the surface area, 0.1 g of resin was treated with 25 mL

of methylene blue of concentration 0.02 g/L. The treatment lasted until there was no further decrease in absorbance. The amount of methylene blue adsorbed was calculated based on concentration difference between the initial and equilibrium values, which were measured by DR 5000 spectrophotometer (HACH) USA. The surface area of the resin was calculated using the following equation:

$$A_s = \frac{GN_{AV} \emptyset 10^{-20}}{M M_W} \quad (3)$$

where A_s is the gel resin surface area in m²/g, G the amount of methylene blue adsorbed (g), N_{AV} the Avogadro's number (6.02×10^{23}), \emptyset the methylene blue molecular cross-section (197.2 Å²), M_W the molecular weight of methylene blue (373.9 g/mol) and M is the mass of adsorbent (g). The surface area of the prepared resins was calculated to be 110 and 126 m²/g for R1 and R2, respectively.

2.3.4. Zeta potential measurements

Zeta potential measurements were performed for resins R1 and R2. A 0.01 g of resin was mixed with 50 mL of 0.1 M KCl. The suspension was then adjusted to the specified pH and kept under stirring for 15 min. After conditioning, the suspension was left for another 15 min for settling before measurements which were performed using zeta sizer 2000 (Malvern Instruments Ltd., London, UK).

2.4. Uptake measurements

2.4.1. Preparation of solutions

The chemical structure of RB5 is shown in Scheme 2. A stock solution of RB5 (1×10^{-3} M) was prepared in distilled water. HCl and NaOH were used to change the acidity of the medium. NH₄OH/NH₄Cl buffer (0.1 M NH₄OH/0.01 M NH₄Cl) was prepared to produce pH 10 and used as an eluent for RB5.

2.4.2. Batch method

2.4.2.1. Effect of pH. Adsorption of the investigated dye on the resins obtained under controlled pH was carried out. 0.1 g of dry resins (R1 or R2) were placed in a series of flasks containing 40 mL of distilled water for 1 h. Thereafter 50 mL of dye solution (2×10^{-3} M) was added to each flask. The desired pH was obtained using HCl or NaOH and the volume of solution in each flask was completed to 100 mL. The contents of the flasks were equilibrated for 3 h on a Vibromatic-384 shaker at 300 rpm and 25 ± 1 °C. The residual concentration of dye was determined spectrophotometrically at 596 nm using DR/2010 spectrophotometer, HACH, USA.

2.4.2.2. Effect of time. A 0.1 g of dry resins (R1 or R2) were swelled in a flask containing 45 mL of distilled water for 1 h. Fifty milliliters of dye solution (2×10^{-3} M) was added to the flask. Few drops of HCl were added to the flask to adjust the initial pH at 3 and the volume of the solution was completed to 100 mL. The initial concentration of the dye becomes (1×10^{-3} M). The contents of the flask were shaken for 3 h on a Vibromatic-384 shaker at 300 rpm and 25 ± 1 °C. Five milliliters of the solution was taken at different time intervals, where the residual concentration of dye was estimated according to the above method.

2.4.2.3. Adsorption isotherms. Complete adsorption isotherms were obtained by soaking 0.1 g of dry resins (R1 or R2) in a series of flasks containing 45 mL of distilled water for 1 h. Fifty milliliters of RB5 solution with different concentrations were added to each flask. The initial pH of each solution was adjusted at 3 and the volume of the solution was completed to 100 mL. The flasks were conditioned at 300 rpm while keeping the temperature at 25, 35, 45 or 55 °C for 3 h. Later on, the residual concentration of the dye was determined following the above method.

2.4.3. Column experiments

Column experiments were performed in a plastic column with a length of 10 cm and a diameter of 1.0 cm. A small amount of glass wool was placed at the bottom of the column to keep the contents. The column was packed with 0.5 g of the investigated resin. Dye solution having an initial concentration of 0.1×10^{-3} M was flowed downward through the column at a desired flow rate. Samples were collected from the outlet of the column at different time intervals and analyzed for dye concentration. The operation of the column was stopped when the outlet dye concentration matches its initial concentration. The outlet dye concentrations were plotted versus time at different flow rates to give the breakthrough curves.

2.4.4. Elution

Elution experiments were performed by placing resin R1 or R2 in a plastic column then loaded up to saturation with RB5 solution (0.1×10^{-3} M) at pH 3. The resin loaded by the dye was then subjected to elution using $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ buffer (pH 10). The concentration of the released dye at 10 mL portions of the down-flow was determined. The elution process continued till the down-flow became free of the dye. The resin was then prepared for the next loading cycle by careful washing with distilled water through the column.

3. Results and discussions

3.1. Characterization of the resins

The infrared bands of the chitosan/pentamine (R1) appeared in close proximity to those of its salt (R2). The most striking difference between the two spectra is the band of the salt positioned at 1483 cm^{-1} (Fig. 1), which corresponds to an asymmetric angular bending of methyl groups of quaternary hydrogen [25].

The amino group concentration of the raw chitosan was calculated from the obtained degree of deacetylation (82.1%) and found to be 4.63 mmol/g. This value is compatible with that determined by volumetric method of HCl (4.35 mmol/g).

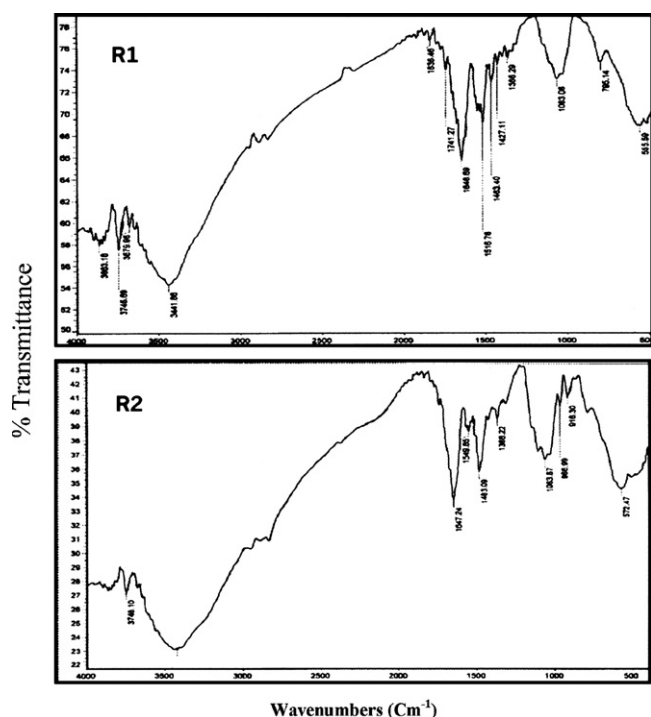


Fig. 1. FT-IR Spectra of R1 and R2 resins.

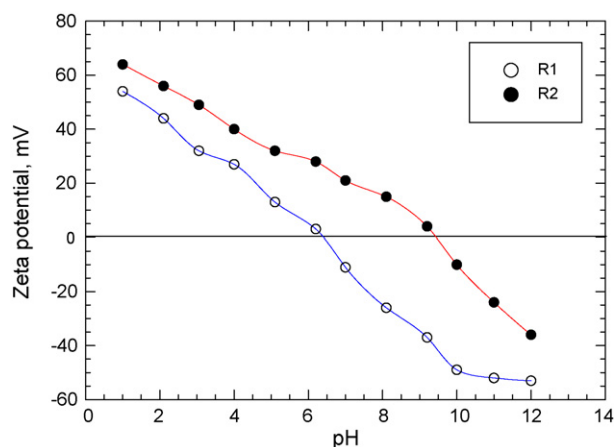


Fig. 2. Zeta potential measurements of R1 and R2 resins, ionic strength 1×10^{-2} M NaCl.

The amine active sites of R1 determined using HCl was found to be 4.9 mmol/g, whereas the quaternary amino group concentration of R2 was 3.5 mmol/g. The lower value of concentration of quaternary amine sites of R2 compared to the amine active sites of R1 may be explained on the basis of not all amine sites are suitable to react GTMAC.

Zeta potential measurements, presented in Fig. 2, indicate that, under acidic conditions, both resins have positive surface charge up to approximately pH of 6.2 and 9.7 (the point of zero charge PZC) for R1 and R2, respectively. At higher pH values, the surface charge reverses to negative. R2 resin showed higher positive charge than R1, this is due to the presence of quaternary amino groups in the resin structure.

3.2. Uptake studies using batch method

The interaction between a dye and chitosan can be affected by the pH of the aqueous medium in two ways:

- The charge of the sulphonate groups of the reactive dye, and its net charge depends on the pH of the solution.
- The surface of chitosan is also pH-dependent, with a pK_a ranging from 6.2 to 6.7 for most chitosans [11], the overall charge may vary with the pH of the solution and the degree of neutralisation of the amine groups.

Therefore, the interaction between dye molecule and chitosan is basically the combined effect of the charges on the dye molecule and the surface of the biopolymer.

The effect of the acidity of the medium on the uptake of dye anions (DSO_3^-) by R1 and R2 is given in Fig. 3. Generally it is seen that, for both resins the maximum uptake value was obtained at pH 3. The observed decrease in the uptake value at $\text{pH} < 3$ for both resins may be attributed to the decrease in dye dissociation which leads to a lower concentration of the anionic dye species available to interact with the resin's active sites. Above pH 3, R1 displays a sharp decrease in the uptake value as pH increases. While R2 shows a slow decrease. This behaviour can be explained on the basis of the lower extent of protonation of amino groups at high pH. The observed higher uptake value of R2 than that of R1 at all pH values may be attributed to the presence of trimethylammonium chloride moiety (strong basic nature) in addition to amine moiety (which only present in R1). The mechanism of interaction of RB5 anions with R1 and R2 can be represented as follows:

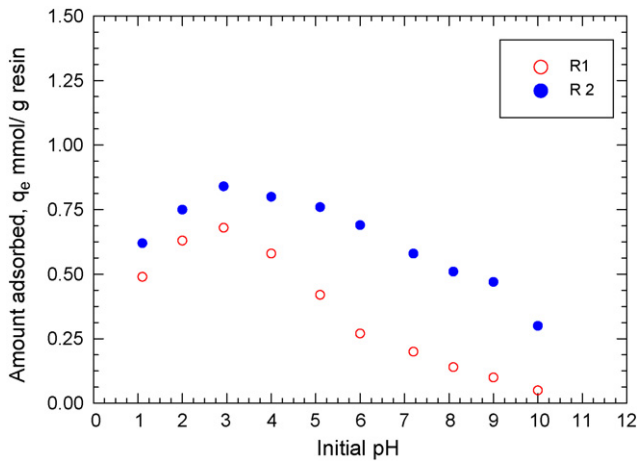
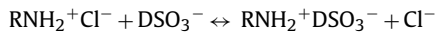


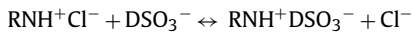
Fig. 3. Effect of pH on the adsorption of RB5 on the chitosan resins at 25 °C and initial concentration of 1×10^{-3} .

For R1:

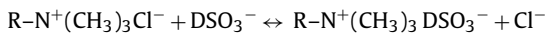


For R2:

(i) in acidic medium



(ii) in neutral and basic media trimethyl ammonium chloride moiety which work as anion exchanger according the following mechanism



It is seen that R1 works efficiently towards the removal of RB5 anions in acidic medium. While R2 works efficiently in all pH ranges (acidic/neutral/basic). It is worth to mention that the equilibrium pH is greater than initial one; this is probably due to the decrease of the acid dye concentration in the aqueous medium.

3.2.1. Kinetic studies

Fig. 4 shows the change in the uptake of RB5 by the given resins as a function of time at initial concentration of 1×10^{-3} M and pH 3. It could be seen that about 90% of the total uptake of RB5 could be achieved within 50 min. The data in Fig. 4 were treated according to pseudo-first and pseudo-second order kinetic models

(i) Pseudo-first order model [26]:

$$q_t = q_e [1 - \exp^{-k_1 t}] \quad (4)$$

where k_1 is the pseudo-first order rate constant (min^{-1}) of adsorption and q_e and q_t (mmol/g) are the amounts of dye adsorbed at equilibrium and time t , respectively.

(ii) Pseudo-second order model [27]:

$$q_t = \frac{k_2 t}{1 + k_2 q_e t} \quad (5)$$

where k_2 is the pseudo-second order rate constant of adsorption ($\text{g mmol}^{-1} \text{min}^{-1}$). The kinetic parameters in both two models are determined from the linear plots of $\log(q_e - q_t)$ versus t for pseudo-first order or (t/q_t) versus t for pseudo-second order. The validity of each model is checked by the fitness of the straight line (r^2) as well as the experimental and calculated values of q_e . Accordingly, and as shown in Table 1, pseudo-second order model is more valid for adsorption process than pseudo-first order one.

Most adsorption reactions take place through multistep mechanism comprising (i) external film diffusion, (ii) intraparticle diffusion and (iii) interaction between adsorbate and active site. Since the first step is excluded by shaking the solution, the rate determining step is one of the other two steps. To know if the intraparticle diffusion is the rate determining step or not the uptake/time

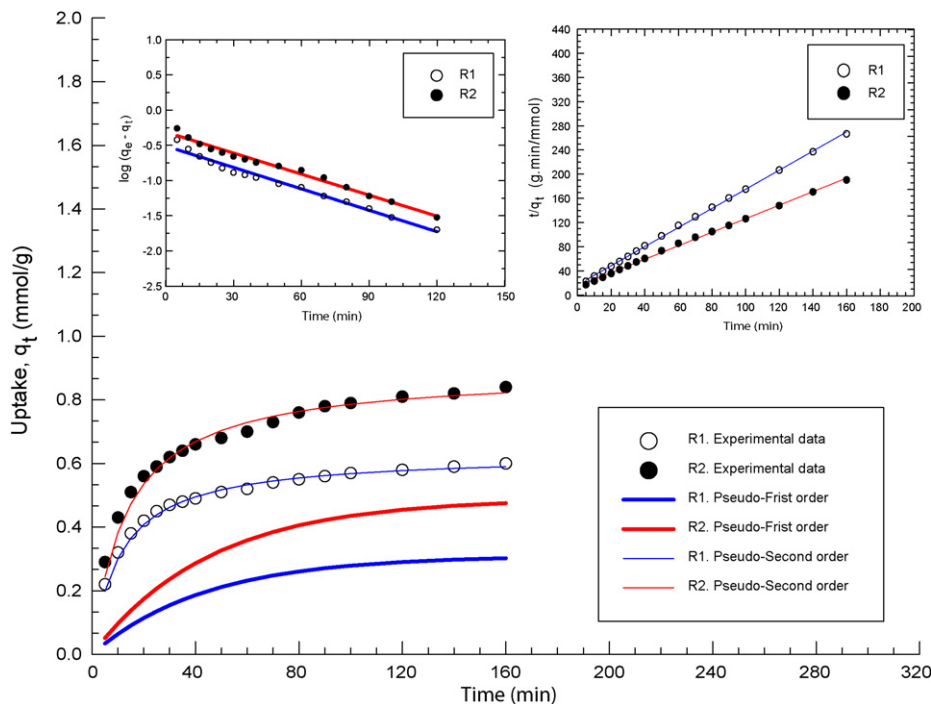


Fig. 4. Pseudo-first-order and pseudo-second order kinetics of the uptake of RB5 anions from initial concentration of 1×10^{-3} by the studied resins at 25 °C and pH 3.

Table 1
Parameters of the pseudo-first order and pseudo-second order for the adsorption of RB5 anions on the studied resin.

Resin	Pseudo-first order			Pseudo-second order			Fickian diffusion low			Elovich equation		
	k_1 (min ⁻¹)	$q_{e,calc}$ (mmol/g)	r^2	k_2 (g/mmol min)	$q_{e,calc}$ (mmol/g)	r^2	K_i (mmol/g min ^{-0.5})	X	r^2	α (mmol g ⁻¹ min ⁻¹)	β (g mmol ⁻¹)	r^2
R1	0.023	0.30	0.977	0.146	0.63	0.999	0.06	0.1	0.949	0.15	7.87	0.981
R2	0.022	0.47	0.985	0.085	0.89	0.998	0.08	0.14	0.946	0.209	5.88	0.985

data was treated according to Fickian diffusion low [28]:

$$q_t = K_i t^{0.5} + X \quad (6)$$

where q_t is the amounts of dye adsorbed at time t and K_i is intraparticle diffusion rate (mmol/g min^{-0.5}). The K_i is the slope of straight-line portions of the plot of q_t versus $t^{0.5}$ (Fig. 5). The K_i values are 0.06 and 0.08 (mmol/g min^{-0.5}) for R1 and R2 respectively. Fig. 5 shows that the straight line portion does not pass through the origin. The small positive values of X (0.1 and 0.14 for R1 and R2 respectively) indicate the limited effect of the boundary layer on the rate of adsorption [29]. This can be explained on the basis of the hydrophobic nature of the multilayer flat aromatic tail of RB5 stacked on the resin surface.

Elovich equation was also applied to the sorption of RB5 by the chitosan resins according to the relation [30]:

$$q_t = 2.303 \frac{1}{\beta} \log(\alpha\beta) + 2.303 \frac{1}{\beta} \log t \quad (7)$$

where q_t is the sorption capacity at time t and α the initial sorption rate (mmol g⁻¹ min⁻¹) and β the desorption constant (g mmol⁻¹). Thus, the constants can be obtained from the slope and intercept of a straight line plot of q_t versus $\log t$. The linearization of the equation giving the rate of reaction allows obtaining the initial sorption rate, α (mmol g⁻¹ min⁻¹) from the intercept of a straight line plot of q_t versus $\ln t$ (Fig. 5). The values of α for the adsorption of RB5 anions on resins R1 and R2 are 0.15 and 0.209 (mmol g⁻¹ min⁻¹), respectively. The values of β were also obtained and are found to be 7.87 and 5.88 g/mmol for R1 and R2, respectively.

3.2.2. Adsorption isotherms

Fig. 7 shows the adsorption isotherms of RB5 by R1 and R2 at different temperatures. It is seen that, for the same equilibrium

concentration the uptake value of R2 is greater than that of R1. This again may be related to the active sites content. The adsorption data of Fig. 6 were treated according to Langmuir and Freundlich models:

$$q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \quad (8)$$

$$q_e = K_F C_e^{1/n} \quad (9)$$

where q_e the adsorbed value of dyes at equilibrium concentration (mmol/g), Q_{max} is the maximum adsorption capacity (mmol/g) and K_L is the Langmuir binding constant which is related to the energy of adsorption (L/mmol), C_e is the equilibrium concentration of dyes in solution (mmol/L). K_F and n are the Freundlich constants related to the adsorption capacity and intensity, respectively.

Plotting C_e/q_e against C_e gives a straight line with slope and intercept equal to $1/Q_{max}$ and $1/K_L Q_{max}$, respectively. The values of K_L and Q_{max} at different temperatures for adsorption of RB5 were obtained from Fig. 6 and reported in Table 2. It is seen that, the value of Q_{max} obtained from Langmuir plots at 25 °C is mainly consistent with that experimentally obtained. This indicates that the adsorption process is mainly monolayer. The experimental data of adsorption of the dye on R1 and R2 are better fit to Langmuir model than Freundlich model. The values of r^2 reported in Table 2 and Table 3, which is a measure of the goodness-of-fit, confirm the good representation of the experimental data by Langmuir model. This indicates the homogeneity of active sites on the surface of R1 and R2. The difference in the values of K_L for R1 and R2 refers the different binding strength and capacity of the dye with the surface of both resins.

The degree of suitability of the obtained resins towards dyes was estimated from the values of the separation factor (R_L) using

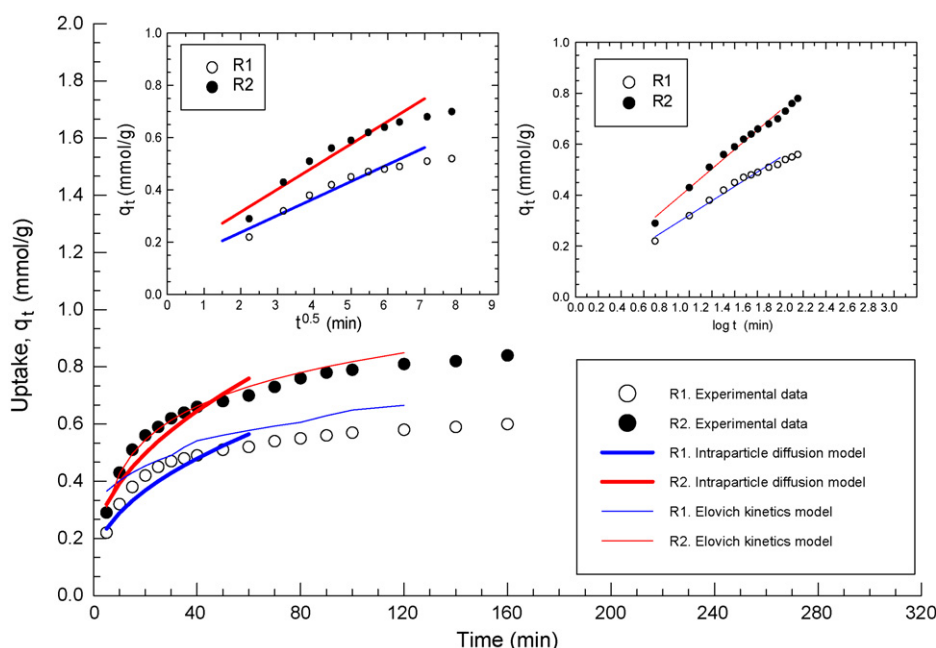


Fig. 5. Intraparticle diffusion and Elovich kinetics of the uptake of RB5 anions from initial concentration of 1×10^{-3} by the studied resins at 25 °C and pH 3.

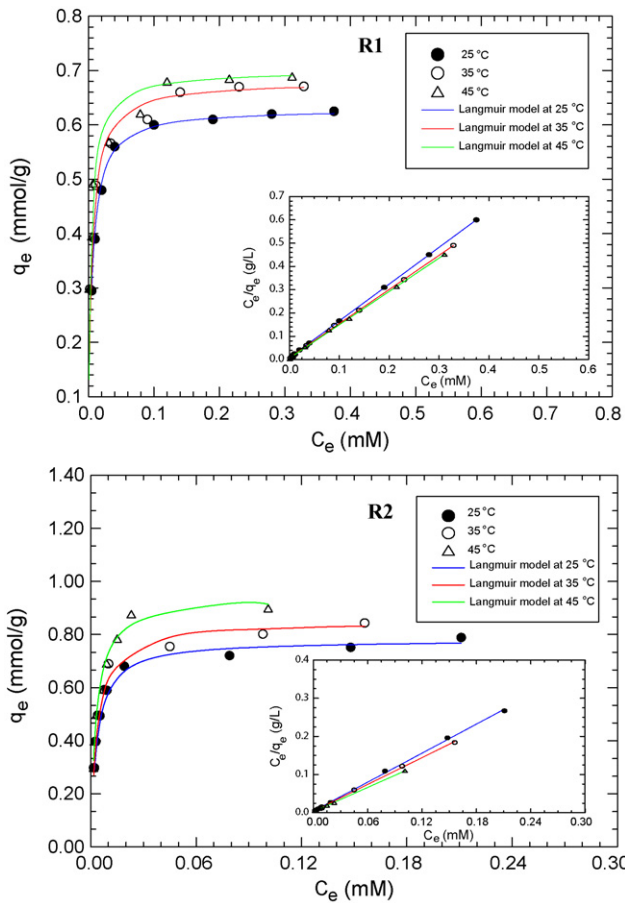


Fig. 6. Langmuir isotherms for the adsorption of RB5 anions by resins R1 and R2 at different temperatures and pH 3.

the following relation [31].

$$R_L = \frac{1}{1 + K_L C_0} \quad (10)$$

where K_L is the Langmuir equilibrium constant and C_0 is the initial concentration of dye. Values of $0 < R_L < 1$ indicates the suitability of the process. The values of R_L for the investigated resins towards the adsorption of RB5 lie between 0.018 and 0.003 for all concentration ranges at 25 °C. This indicates the suitability of resins for RB5 adsorbation.

The comparable values of K_L for both resins at the same temperature may be related to the same mechanism of interaction (anion exchange). The values of K_L at different temperatures were processed according to the following van't Hoff equation [32] to obtain the thermodynamic parameters of the adsorption process

$$\ln K_L = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (11)$$

where ΔH° and ΔS° are enthalpy and entropy changes, respectively, R is the universal gas constant (8.314 J/molK) and T is the absolute temperature (in Kelvin). Plotting $\ln K_L$ against $1/T$ gives a

Table 2
Langmuir constants for adsorption of RB5 anions on the studied resins.

Temperature (°C)	R1				R2			
	$Q_{max, exp}$ (mmol/g)	$Q_{max, calc}$ (mmol/g)	K_L (L/mmol)	r^2	$Q_{max, exp}$ (mmol/g)	$Q_{max, calc}$ (mmol/g)	K_L (L/mmol)	r^2
25	0.62	0.63	181.26	0.999	0.78	0.78	293.05	0.999
35	0.67	0.68	184.12	0.999	0.84	0.85	292.85	0.999
45	0.69	0.70	231.76	0.999	0.90	0.94	352.00	0.999

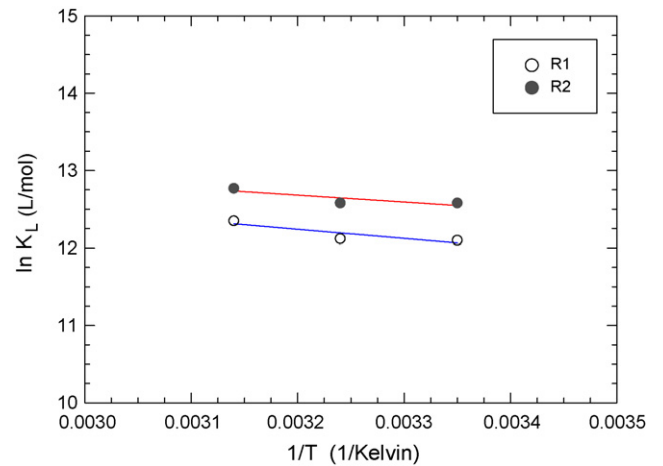


Fig. 7. van't Hoff plots for the uptake of RB5 anions on the studied resins.

Table 3
Freundlich constants for adsorption of RB5 anions on the studied resins.

R1	R2				
	n	K_F	r^2		
6.36	0.80	0.851	5.78	1.12	0.824
6.41	0.87	0.921	5.10	1.34	0.834
6.94	0.88	0.937	3.86	2.04	0.841

Table 4
Enthalpy and entropy changes for adsorption of RB5 anions on the studied resins.

Resin	ΔH° (kJ/mol)	ΔS° (J/molK)
R1	9.75	132.99
R2	7.39	129.10

Table 5
Free energy change for adsorption of RB5 anions on the studied resins at different temperatures.

Temperature (K)	R1		R2	
	ΔG° (kJ/mol)	$T\Delta S^\circ$ (kJ/mol)	ΔG° (kJ/mol)	$T\Delta S^\circ$ (kJ/mol)
298	-29.88	39.63	-31.08	38.47
308	-31.21	40.96	-32.37	39.76
318	-32.54	42.29	-33.66	41.05

straight line with slope and intercept equal to $-\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively. The values of ΔH° and ΔS° were calculated from Fig. 7 and reported in Table 4. The positive values of ΔH° indicate the endothermic nature of adsorption process. The positive values of ΔS° suggest the increased randomness during the adsorption of RB5. The source of this entropy gain is due to liberation of water molecules from the hydrated shells of the sorbed species [33]. Gibbs free energy of adsorption (ΔG°) was calculated from the following relation and given in Table 5

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

The negative values of ΔG° obtained indicate that the adsorption reaction is spontaneous. The observed increase in negative values of ΔG° with increasing temperature may be attributed to the dehydration effect of both dye and active sites, which facilitates the interaction between them [33]. This dehydration effect at elevated temperature may also be reflected in the values of K_L . The values of K_L increase as the temperature increases, indicating higher affinity of the resins towards RB5 at higher temperature. The data given in Table 5 also show an increase in the values of $T\Delta S^\circ$ with increasing temperature and $|T\Delta S^\circ| > |\Delta H^\circ|$. This indicates that the adsorption process is dominated by entropic rather than enthalpic changes [33].

3.3. Column studies

3.3.1. Effect of flow rate

The breakthrough curves of the studied resin towards adsorption of RB5 at different flow rates (1, 2 and 4 mL/min) and a fixed bed height of 1.5 cm are shown in Fig. 8, respectively. Breakthrough and exhaustion occurred faster at higher flow rates. Also as the flow rate increases, RB5 concentration in the effluent increases rapidly resulting in much sharper breakthrough curves. This behaviour may be attributed to the insufficient residence time of the RB5 anions on the column, which negatively affects the interaction process as well as the diffusion of anions through the pores of resin.

3.3.2. Effect of bed height

The data of the effect of bed height of resin on the uptake of the dye are reported in Table 6. As shown in Fig. 9, the bed height was varied from 3.0 to 7.0 cm while the flow rate was held constant at 4 mL/min. The influence of bed height was well checked in terms of breakthrough time (t_b) and service time (t_s). Both parameters (t_b) and (t_s) were increased by increasing the bed height. Generally, the removal efficiency of the resins were significantly affected by the bed height and found to be directly proportional to it. Bed depth service time model (BDST) is a simple model, in which the bed height (Z) and service time (t_s) of the column are linearly related as given in the following equation [34].

$$t_s = \frac{N_0 Z}{C_0 v} - \frac{1}{K_a C_0} \ln \left(\frac{C_0}{C_t} - 1 \right) \quad (13)$$

where C_0 (mmol/L) is the initial dye concentration, C_t (mmol/L) is the dye concentration at the service time just before equivalence to the initial concentration ($C_t/C_0 = 99/100$), N_0 is the total adsorption capacity (mmol of solute/L of sorbent bed), v the linear velocity (cm/h) and K_a characterizes the rate constant of transfer (L/mmol h). The values of N_0 and K_a was calculated from the slope and intercept of the BDST plots, respectively. If K_a is large, even a short bed will avoid breakthrough, but if K_a is small a progressively longer bed is required to avoid breakthrough. The values of K_a for R1 and R2 are 11.89 and 12.67 (L/mmol h), respectively. Again the observed higher K_a value for R2 is consistent with its longer breakthrough time than

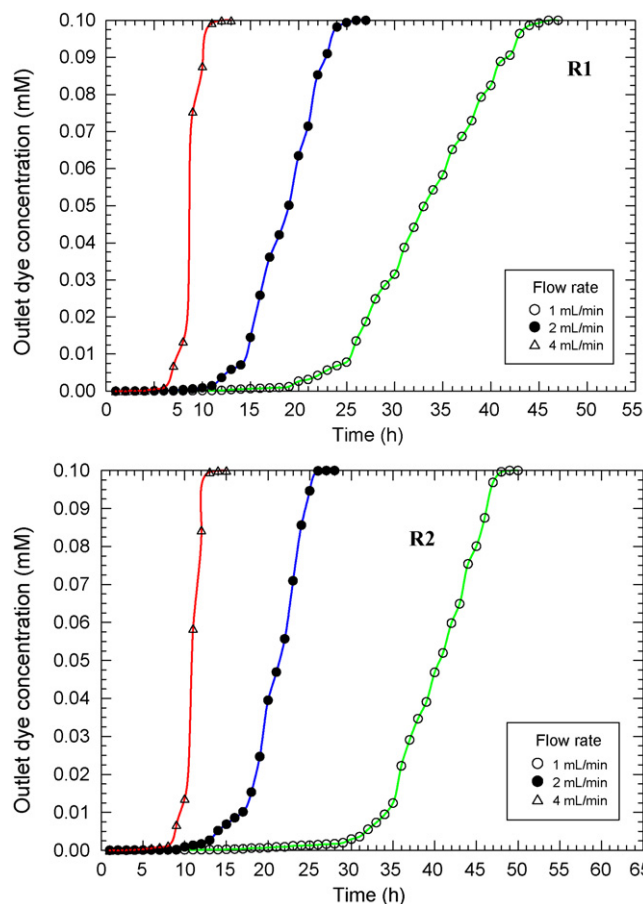


Fig. 8. Effect of flow rate on breakthrough curves for the uptake of RB5 anions by resins R1 and R2 from initial concentration of 0.1×10^{-3} M and pH 3.

that of R1. The critical bed height (Z_0) can be calculated by setting $t_s = 0$ in Eq. (13) [34].

$$Z_0 = \frac{v}{K_a N_0} \ln \left(\frac{C_0}{C_b} - 1 \right) \quad (14)$$

where C_b is the dye concentration at the breakthrough point (mmol/L). The above equation implies that Z_0 depends on the kinetics of the sorption process, the residence time of the solute and the sorption capacity of the resin [34]. The critical bed height for R1 and R2 columns were calculated as 0.68 and 0.45 cm, respectively.

3.3.3. Resin regeneration

Fig. 10 shows the desorption of RB5 anions from resins R1 and R2 using 100 mL of $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ buffer (pH 10) as eluent. As shown in Fig. 10 the highest RB5 concentration was detected in the effluent after flowing 30 mL of 0.1 M ammonia buffer then the concentration

Table 6

Data of column studies for the uptake of RB5 anions by R1 and R2 at different bed heights and flow rates.

Resin	Bed height (cm)	Flow rate (mL/min)	t_s (h)	t_b (h)	K_a (L/mmol h)	N_0 (mmol/L)	Z_0 (cm)	r^2
R1	1.5	1	44	7.0	11.89	172.3	0.68	0.961
	1.5	2	24	5.0				
	1.5	4	11	3.0				
	3	4	23	5.25				
	5	4	31	9.50				
R2	1.5	1	47	7.15	12.67	243.6	0.45	0.927
	1.5	2	25	6.20				
	1.5	4	13	3.20				
	3	4	32	4.60				
	5	4	41.5	14				

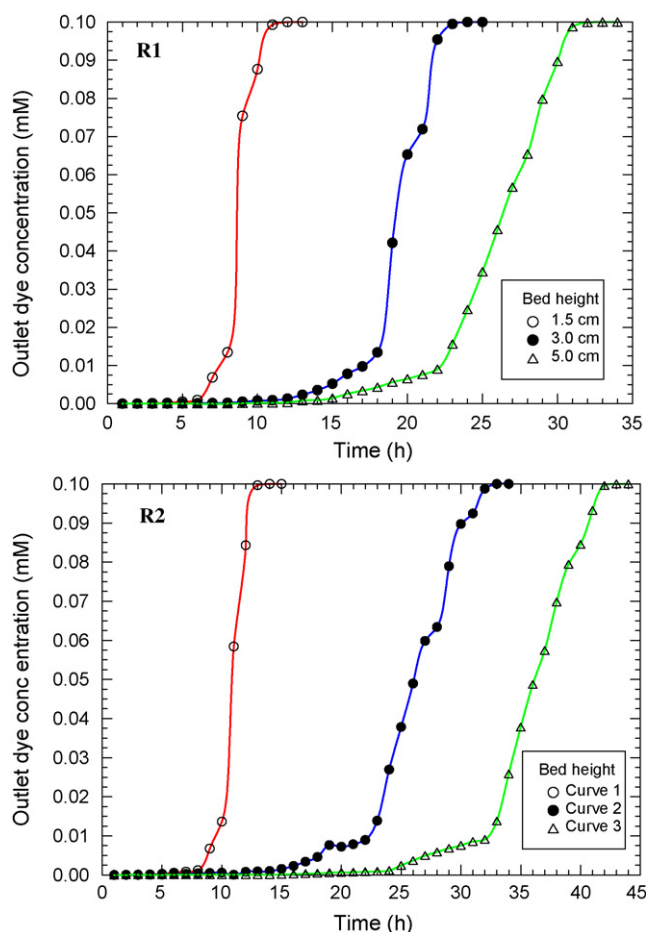


Fig. 9. Effect of bed height on breakthrough curves for the uptake of RB5 anions by resins R1 and R2 from initial concentration of 0.1×10^{-3} M and pH 3.

of RB5 gradually decreased until zero concentration after flowing 90 mL of the eluent. The desorption ratio was calculated using the following equation

$$\text{Desorption ratio (\%)} = \frac{\text{Amount of dye desorbed to the elution medium}}{\text{Amount of dye sorbed on the resin}} \times 100$$

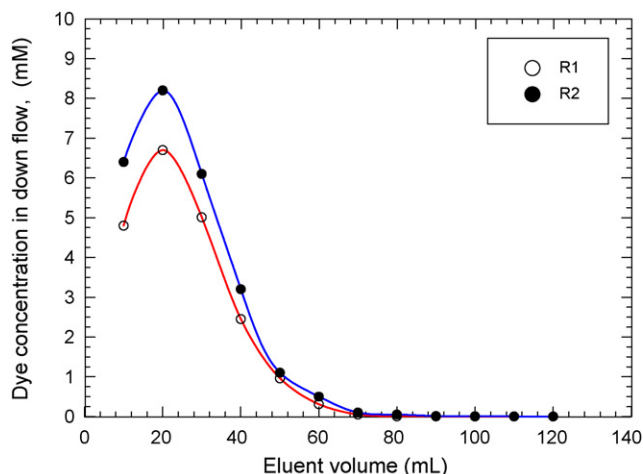


Fig. 10. Elution of RB5 anions from resins R1 and R2 using 0.1 M ammonia buffer.

Both resins showed high desorption ratio ≈ 96 and 97% for R1 and R2, respectively over 3 cycles.

3.4. Conclusions

Removal of RB5 anions from aqueous solutions was studied using magnetic resin derived from chemically modified chitosan. The nature of interaction between the anions and the resin was found to be dependent upon the acidity of the medium. The removal process was carried out through batch and column methods. Kinetic studies referred that the adsorption reaction is pseudo-second order. Thermodynamic parameters obtained indicated that the adsorption process is an endothermic spontaneous reaction and proceeds according to Langmuir isotherm. The resin was regenerated effectively using $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ buffer (pH 10).

Acknowledgements

The author acknowledges the moral support of H.K. Yassen.

References

- I.M. Banat, P. Nigam, D. Singh, R. Marchant, Microbial decolorization of textile-dye-containing effluents: a review, *Bioresour. Technol.* 58 (1996) 217–227.
- T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, *Bioresour. Technol.* 77 (2001) 247–255.
- C.I. Pearce, J.R. Lloyd, J.T. Guthrie, The removal of colour from textile wastewater using whole bacterial cells: a review, *Dyes Pigments* 58 (2003) 179–196.
- G. McMullan, C. Meehan, A. Conneely, N. Kirby, T. Robinson, P. Nigam, I.M. Banat, R. Marchant, W.F. Smyth, Microbial decolourisation and degradation of textile dyes, *Appl. Microbiol. Biotechnol.* 56 (2001) 81–87.
- X. Yang, B. Al-Duri, Application of branched pore diffusion model in the adsorption of reactive dyes on activated carbon, *Chem. Eng. J.* 83 (2001) 15–23.
- T.O. Mahony, E. Guibal, J. Tobin, Reactive dye biosorption by *Rhizopus arrhizus* biomass, *Enzyme Microb. Technol.* 31 (2002) 456–463.
- S. Wang, H. Li, X. Longya, Application of zeolite MCM-22 for basic dye removal from wastewater, *J. Colloid Interface Sci.* 295 (2006) 71–80.
- N. Sakkayawong, P. Thiravetyan, W. Nakbanpote, Adsorption mechanism of synthetic reactive dye wastewater by chitosan, *J. Colloid Interface Sci.* 286 (2005) 36–42.
- L.C. Morais, O.M. Freitas, E.P. Goncalves, L.T. Vasconcelos, G.C.G. Beca, Reactive dyes removal from wastewaters by adsorption on eucalyptus bark: variables that define the process, *Water Res.* 33 (1999) 979–998.
- M.S. Chiou, G.S. Chuang, Competitive adsorption of dye metanil yellow and RB15 in acid solutions on chemically cross-linked chitosan beads, *Chemosphere* 62 (2006) 731–740.
- A. Szyguła, E. Guibala, M. Ruiz, A.M. Sastrec, The removal of sulphonated azo-dyes by coagulation with chitosan, *Colloid Surf. A: Physicochem Eng. Aspects* 330 (2008) 219–226.
- I. Uzun, Kinetics of the adsorption of reactive dyes by chitosan, *Dyes Pigments* 70 (2006) 76–83.
- G. Gibbs, J.M. Tobin, E. Guibal, Influence of chitosan preprotonation on Reactive Black 5 sorption isotherms and kinetics, *Ind. Eng. Chem. Res.* 43 (2004) 1–11.
- S. Karcher, A. Kornmüller, M. Jekel, Anion exchange resins for removal of reactive dyes from textile wastewaters, *Water Res.* 36 (2002) 4717–4724.
- M.M. Nassar, M.S. El-Geundi, Comparative cost of colour removal from textile effluents using natural adsorbents, *J. Chem. Technol. Biotechnol.* 50 (1991) 257–264.
- F.S.C. dos Anjos, E.F.S. Vieira, A.R. Cestari, Interaction of indigo carmine dye with chitosan evaluated by adsorption and thermochemical data, *J. Colloid Interface Sci.* 253 (2002) 243–246.
- B.A. Utkelov, E.E. Ergozhin, R.K. Ashkeeva, Selective chelating ion exchange resins containing α -dithiol groups part 1. Synthesis, *React. Polym.* 14 (1991) 187–191.
- A.M. Donia, A.A. Atia, H.A. El-Boraey, D. Mabrouk, Adsorption of Ag(I) on glycidyl methacrylate/*N,N'*-methylene bis-acrylamide chelating resins with embedded iron oxide, *Sep. Purif. Technol.* 48 (2006) 281–287.
- A.M. Donia, A.A. Atia, H.A. El-Boraey, D. Mabrouk, Uptake studies of copper(II) on glycidyl methacrylate chelating resin containing Fe_2O_3 particles, *Sep. Purif. Technol.* 49 (2006) 64–70.
- A.A. Atia, A.M. Donia, A.E. Shahin, Studies on the uptake behavior of a magnetic Co_3O_4 -containing resin for Ni(II), Cu(II) and Hg(II) from their aqueous solutions, *Sep. Purif. Technol.* 46 (2005) 208–213.
- A.M. Donia, A.A. Atia, K.Z. Elwakeel, Removal of gold(III) and silver(I) on a chemically modified chitosan with magnetic properties, *Hydrometallurgy* 87 (2007) 197–206.
- Y.K. Sun, M. Ma, Y. Zhang, N. Gu, Synthesis of nanometer-size maghemite particles from magnetite, *Colloids Surf. A* 245 (2004) 15–19.

- [23] A.G.S. Prado, J.D. Torres, E.A. Faria, S.C.L. Dias, Comparative adsorption studies of indigo carmine dye on chitin and chitosan, *J. Colloid Interface Sci.* 277 (2004) 43–47.
- [24] A.A. Atia, A.M. Donia, S.A. Abou-El-Enein, A.M. Yousif, Studies on uptake behaviour of copper(II) and lead(II) by amine chelating resins with different textural properties, *Sep. Purif. Technol.* 33 (2003) 295–301.
- [25] V.A. Spinelli, M.C.M. Laranjeira, V.T. Favere, Preparation and characterization of quaternary chitosan salt: adsorption equilibrium of chromium(VI) ion, *React. Funct. Polym.* 61 (2004) 347–352.
- [26] S. Lagergren, Zur theorie der sogenannten adsorption gelosterstoffe. *Kungliga Svenska Vetenskapsakademiens, Handlingar* 24 (1898) 1–39.
- [27] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process. Biochem.* 34 (1999) 451–465.
- [28] M.Y. Chang, R.S. Juang, Adsorption of tannic acid, humic acid, and dyes from water using the composite of chitosan and activated clay, *J. Colloid Interface Sci.* 278 (2004) 18–25.
- [29] A.M. Donia, A.A. Atia, A.M. Heniesh, Efficient removal of Hg(II) using magnetic chelating resin derived from copolymerization of bithiourea/thiourea/glutaraldehyde, *Sep. Purif. Technol.* 60 (2008) 46–53.
- [30] M.A. Abd El-Ghaffar, Z.H. Abdel-Wahab, K.Z. Elwakeel, Extraction and separation studies of silver(I) and copper(II) from their aqueous solution using chemically modified melamine resins, *Hydrometallurgy* 96 (1–2) (2009) 27–34.
- [31] L. Qi, Z. Xu, Lead sorption from aqueous solutions on chitosan nanoparticles, *Colloids Surf. A* 251 (2004) 186–193.
- [32] J. Tellinghuisen, Van't Hoff analysis of K° (T): How good or bad? *Biophys. Chem.* 120 (2006) 114–120.
- [33] A.M. Donia, A.A. Atia, K.Z. Elwakeel, Selective separation of mercury(II) using magnetic chitosan resin modified with Schiff's base derived from thiourea and glutaraldehyde, *J. Hazard. Mater.* 151 (2008) 372–379.
- [34] G.S. Bohart, E.Q. Adams, Some aspects of the behavior of charcoal with respect to chlorine, *J. Am. Chem. Soc.* 42 (1920) 523–544.