

Efficient removal of Reactive Black 5 from aqueous media using glycidyl methacrylate resin modified with tetraethelenepentamine

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ABSTRACT

Glycidyl methacrylate/methelenebisacrylimide resin loaded with tetraethelenepentamine ligand was prepared and investigated. The adsorption characteristics of the obtained resin towards Reactive Black 5 (RB5) from aqueous solutions at different experimental conditions were established by means of batch and column methods. The mechanism of interaction between RB5 and resin's active sites was discussed. The resin showed high affinity for the adsorption of RB5 where an uptake value of 0.63 mmol/g was reported for the obtained resin, at 25 °C. The kinetics and thermodynamic behavior of the adsorption reaction were also defined. These data indicated an endothermic spontaneous adsorption process and kinetically followed the pseudo-second order model. Breakthrough curves for the removal of RB5 were studied at different flow rates and bed heights. The critical bed height for the studied resin column was found to be 0.764 cm at flow rate of 8 mL/min. The adsorbed dye was eluted from the investigated resin effectively. Regeneration and durability of the loaded resin towards the successive resin were also clarified.

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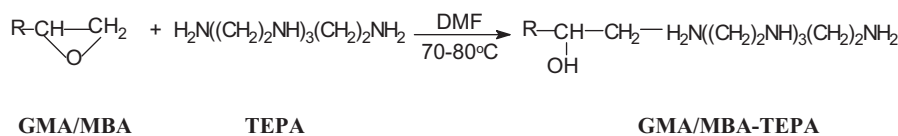
1. Introduction

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]. Unless coloring materials are properly removed, dye wastewater significantly affects photosynthetic activity in aquatic life due to reduced light penetration [7]. Conventional methods for the removal of dyes in effluents include

physical, chemical, and biological processes [8]. Unfortunately, reactive dyes are resistant to bacterial activity and biological treatment alone will take a long time to be effective [9]. Furthermore, it is difficult to remove reactive dyes using chemical coagulation due to the dye's high solubility in water [10]. 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 [11–15]. 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 [16]. Recently, chelating resins represent an important category of promising adsorbents. They are highly selective, efficient and easily regenerable relative to other adsorbent materials [17,18]. Recently, the use of chelating and chelating resins for the removal of some dyes from aqueous solutions was reported by many authors [19–21]. The ultimate goal of this study is to develop new adsorbent based on glycidyl methacrylate for the removal of Reactive Black 5 (RB5) from aqueous solutions. The CI Reactive Black 5 is one of the common reactive dyes and was chosen as a target pollutant. It has high metamery (have shade differences under different light conditions) and high thermal sensitive properties. The photocatalytic degradation of RB5 is a complicated process with a mechanism involving several chemical and photocatalytic stages and a great number of inter-

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Scheme 1. Reaction of GMA/MBA resin with TEPA.

mediates. The interaction of the Reactive Black 5 dye with the glycidyl methacrylate resin results in the formation of mixed colloids (dye/resin) that can settle after a long contact time or can be recovered (after maturation) by filtration. Protonated amino groups neutralize anionic charges of the dye (coagulation effect), before neutralized dyes aggregate and settle (flocculating effect) [22–24]. The factors affecting the removal behavior will be studied. Thermodynamic as well as kinetic properties of the removal process will also be clarified.

2. Experimental

2.1. Dye

Reactive Black 5 was supplied by Aldrich and used as received. This dye is characterized as a diazo compound bearing 4 sulphonyl groups (Scheme 2), Mr 991.82 g/mol. The characteristic wavelength of absorbance of RB5 is 597.6 nm, which is responsible for the dark blue color arising from aromatic rings connected by azo groups.

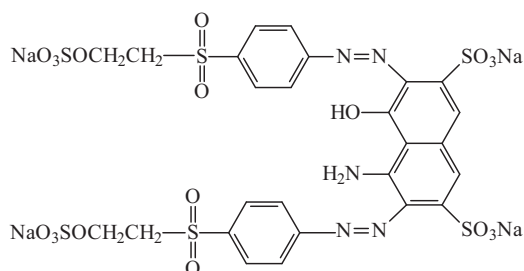
2.2. Chemicals

Glycidyl methacrylate (GMA), *N,N'*-methylenebisacrylamide (MBA) and benzoyl peroxide (Bz_2O_2) were Aldrich products. All other chemicals were Prolabo products and were used as received.

2.3. Preparation of resin

Glycidyl methacrylate/methylenebisacrylamide (GMA/MBA) resin was prepared according to the previously reported method [21]. Glycidyl methacrylate (GMA) was polymerized in the presence of methylenebisacrylamide (MBA) as a cross-linking agent at a weight ratio of 9.9:0.1, respectively. A 0.1 g Bz_2O_2 (initiator) was added to the mixture of GMA/MBA with stirring. One milliliter isopropyl alcohol and 12.6 mL cyclohexane were mixed and then added to the former solution. All the contents were then poured into a flask containing 73 mL (1%) polyvinyl alcohol and heated on a water bath at 70–80 °C with continuous stirring for 3 h. A heavy white precipitate was formed, filtered off and washed with methanol to remove the unreacted materials and then dried in air.

The GMA/MBA resin obtained above was loaded by tetraethylene-pentamine (TEPA) as follows: one gram of the resin was added to 2 g of TEPA dissolved in 12 mL DMF. The reaction mixture was refluxed at 75–80 °C for 72 h in an oil bath.



Scheme 2. Chemical structure of Reactive Black 5.

The product obtained was filtrated off, washed with methanol and then dried in air and referred as GMA/MBA-TEPA (Scheme 1).

The concentration of amino group on GMA/MBA-TEPA resin was estimated using a volumetric method [25]. A 100 mL of 0.05 M HCl solution was added to 0.5 g resin and conditioned for 15 h on a Vibromatic-384 Shaker, Gallenkamb, England. The residual concentration of HCl was estimated through the titration against 0.05 M NaOH solution and phenolphthalein as indicator.

Concentration of amino group

$$= \frac{(M_1 - M_2) \times 100}{0.5} \text{ (mmol/g of resin)} \quad (1)$$

where M_1 and M_2 are the initial and final concentrations of HCl.

2.4. Characterization of the resin

2.4.1. 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 value is ($24 \pm 3\%$), with insignificant differences when changing conditions. This value reflects the hydrophilic character of the resin type.

2.4.2. Surface area

The surface area of the prepared resin was measured by methylene blue adsorption method as reported previously [26]. 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:

$$A_s = \frac{G N_{Av} \emptyset 10^{-20}}{MM_w} \quad (3)$$

where A_s is the gel resin surface area in m^2/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 \AA^2), MM_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 resin was calculated to be $90 \text{ m}^2/\text{g}$.

2.4.3. Zeta potential measurements

Zeta potential measurements were performed for the prepared resin. 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).

2.5. Uptake measurements

2.5.1. Preparation of solutions

A stock solution of RB5 (1×10^{-3} M) was prepared in distilled water, the structure of RB5 is shown in Scheme 2. HCl and NaOH were used to change the acidity of the medium. A stock solution of NaOH (1 M) was prepared to be used as an eluent for RB5.

2.5.2. Batch method

(i) Effect of pH

Adsorption of the investigated dye on the resin obtained under controlled pH was carried out. 0.1 g of dry resin was 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 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.

(ii) Effect of time

A 0.1 g of dry resin was 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 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.

(iii) Adsorption isotherms

Complete adsorption isotherms were obtained by soaking 0.1 g of dry resin 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.

2.5.3. 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.

2.5.4. Elution

Elution experiments were performed by placing 1.0 g of GMA/MBA-TEPA resin 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 different concentrations of NaOH at flow rate of 2 mL/min. The concentration of the

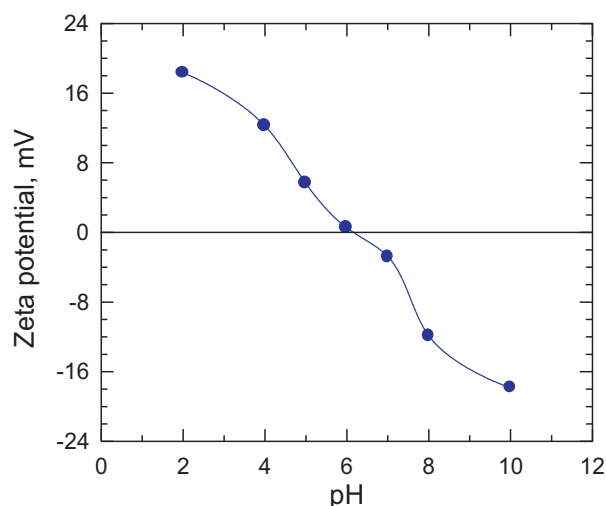


Fig. 1. Zeta potential measurements of GMA/MBA-TEPA resin, ionic strength 1×10^{-2} M NaCl.

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 resin

The amine active sites determined for the prepared resin was found to be 4.6 mmol/g.

Zeta potential measurements, presented in Fig. 1, indicate that, under acidic conditions, the resin has positive surface charge up to approximately pH of 6.1 (the point of zero charge PZC). At higher pH values, the surface charge reverses to negative. This is due to the presence of amino groups in the resin structure.

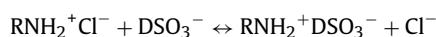
3.2. Uptake studies using batch method

The interaction between a dye and GMA resin 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 depend on the pH of the solution.
- The surface of GMA/MBA-TEPA resin is also pH-dependent. The overall charge may vary with the pH of the solution and the degree of the protonation of the amine groups.

Therefore, the interaction between dye molecule and GMA/MBA-TEPA resin is basically the combined effect of the charges on the dye molecule and the surface of the resin.

The effect of the acidity of the medium on the uptake of dye anions (DSO_3^-) by GMA/MBA-TEPA resin is given in Fig. 2. Generally, it is seen that, the maximum uptake value was obtained at pH 3. The observed decrease in the uptake value at $\text{pH} < 3$ 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 $\text{pH} = 3$, GMA/MBA-TEPA resin displays a sharp decrease in the uptake value as pH increases. This behavior can be explained on the basis of the lower extent of protonation of amino groups at high pH. The mechanism of interaction of RB5 anions with GMA/MBA-TEPA resin can be represented as follows:



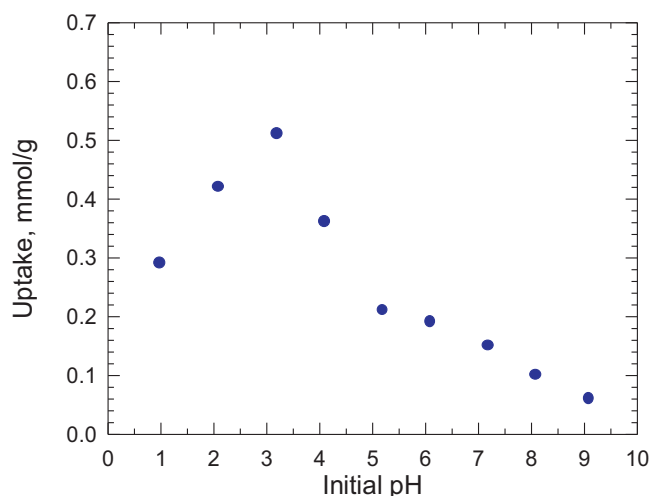


Fig. 2. Effect of pH on the adsorption of RB5 onto GMA/MBA-TEPA at 25 °C and initial concentration of 1×10^{-3} .

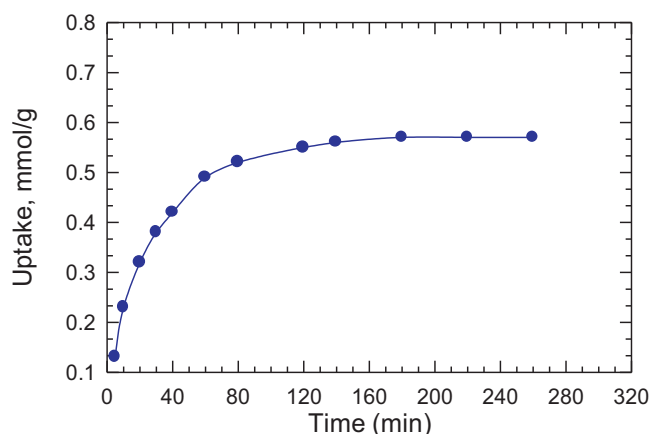


Fig. 3. Adsorption of RB5 as a function of time onto GMA/MBA-TEPA at 25 °C and initial concentration of 1×10^{-3} .

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. 3 shows the change in the uptake of RB5 by the given resin 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 60 min. The data in Fig. 3 were treated according to pseudo-first and pseudo-second order kinetic models.

(i) Pseudo-first order model [27]:

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

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 [28]:

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

where k_2 is the pseudo second order rate constant of adsorption (g/mmol/min). The kinetic parameters in both two models are determined from the linear plots of $\log(q_e - q_t)$ vs t for pseudo-first order or (t/q_t) vs t for pseudo-second order (Fig. 4). The validity of

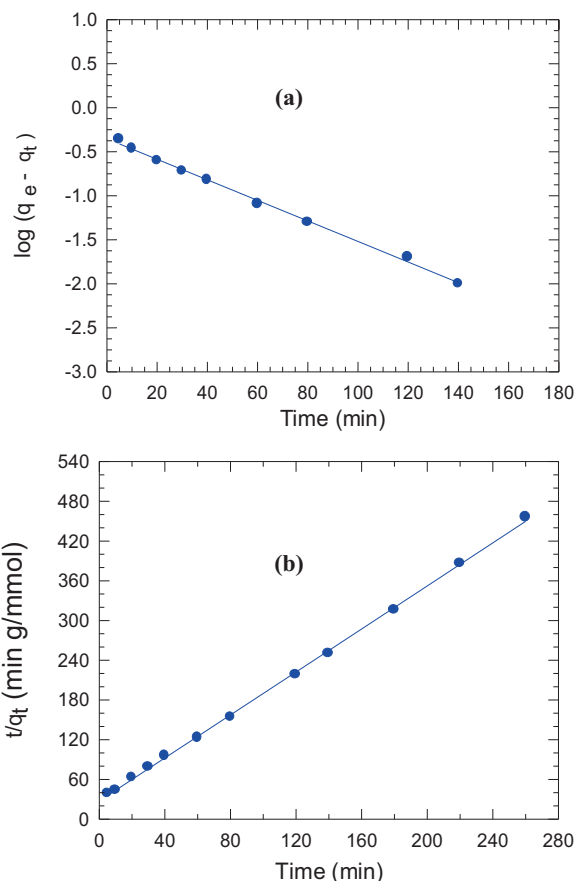


Fig. 4. (a) Pseudo first-order and (b) Pseudo second-order kinetics of the uptake of RB5 anions from initial concentration of 1×10^{-3} by the studied resins at 25 °C and pH 3.

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 data was treated according to Fickian diffusion law [29]:

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

where q_t is the amounts of dye adsorbed at time t and K_i is intraparticle diffusion rate ($\text{mmol/g min}^{-0.5}$). The K_i is the slope of straight-line portions of the plot of q_t vs $t^{0.5}$ (Fig. 5a). The K_i value is 0.056 ($\text{mmol/g min}^{-0.5}$). Fig. 5a shows that the straight line portion does not pass through the origin. The small positive values of X (0.061) indicate the limited effect of the boundary layer on the rate of adsorption [30]. 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 GMA/MBA-TEPA resin according to the relation [31]:

$$q_t = 2.3031/\beta \log(\alpha\beta) + 2.3031/\beta \log t \quad (8)$$

where q_t is the sorption capacity at time t and α the initial sorption rate (mmol/g/min) and β the desorption constant (g/mmol). Thus,

Table 1
Parameters of the pseudo-first order and pseudo-second order for the adsorption of RB5 anions on the studied 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/min)	β (g/mmol)	r^2
0.0268	0.4434	0.996	0.0958	0.616	0.999	0.056	0.061	0.992	0.069	7.012	997

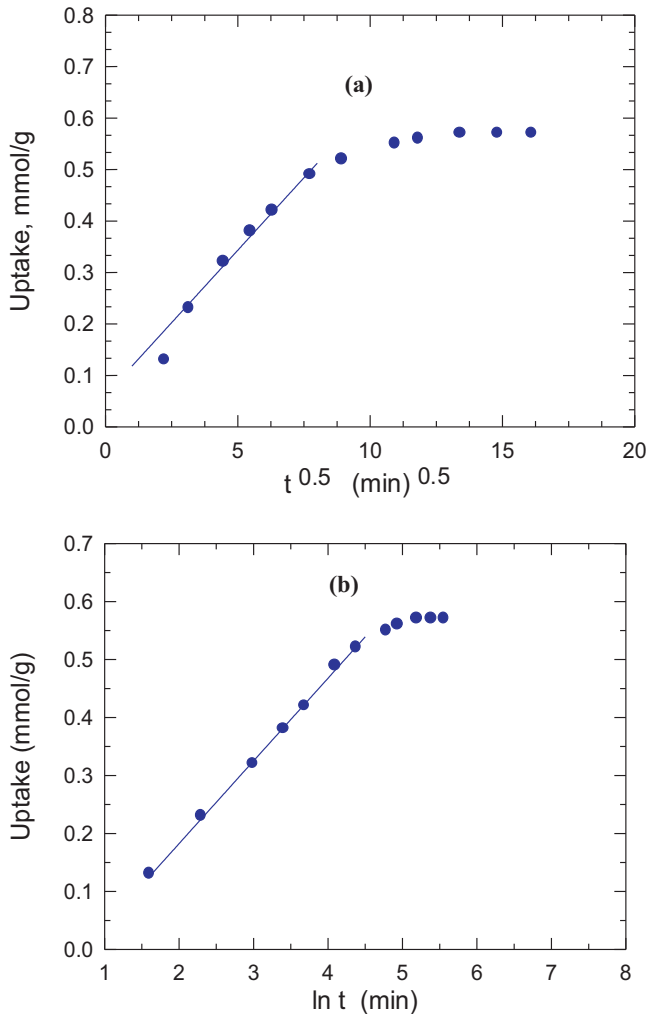


Fig. 5. (a) Intraparticle diffusion and (b) Elovich kinetics of the uptake of RB5 anions from initial concentration of 1×10^{-3} by the studied resins at 25 °C and pH 3

the constants can be obtained from the slope and intercept of a straight line plot of q_t vs $\log t$. The linearization of the equation giving the rate of reaction allows obtaining the initial sorption rate, α (mmol/g/min) from the intercept of a straight line plot of q_t vs $\ln t$ (Fig. 5b). The value of α for the adsorption of RB5 anions on resin is 0.069 (mmol/g/min), where as the value of β was found to be 7.012 g/mmol.

3.2.2. Adsorption isotherms

Fig. 6 shows the adsorption isotherms of RB5 by GMA/MBA-TEPA resin at different temperatures. The experimental data of Fig. 6 were treated according to Langmuir and Freundlich models (Fig. 7):

$$q_e = \frac{Q_{max}K_L C_e}{1 + K_L C_e} \quad (9)$$

$$q_e = K_F C_e^{1/n} \quad (10)$$

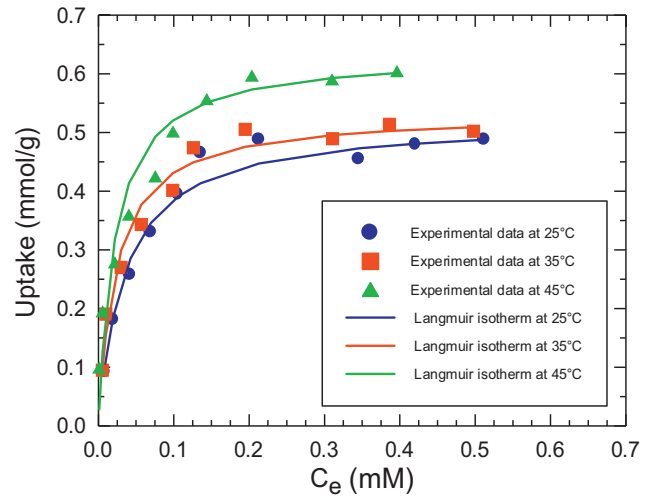


Fig. 6. Non linear Langmuir isotherms for the adsorption of RB5 anions by GMA/MBA-TEPA at different temperatures and pH 3.

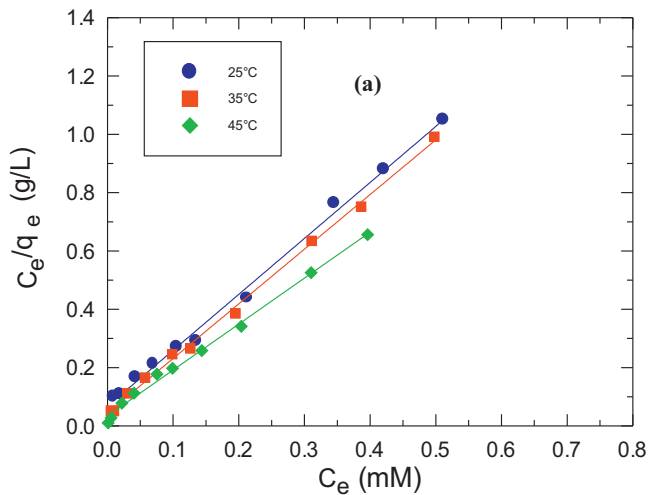


Fig. 7. linear Langmuir isotherms for the adsorption of RB5 anions by GMA/MBA-TEPA at different temperatures and pH 3.

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. 7 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 GMA/MBA-TEPA resin are better fit to Langmuir model (Fig. 7) than Freundlich model. The values of r^2

Table 2
Langmuir and Freundlich constants for adsorption of RB5 anions on the studied resin.

Temperature (°C)	Langmuir constants				Freundlich constants		
	$Q_{\max, \text{exp}}$ (mmol/g)	$Q_{\max, \text{calc}}$ (mmol/g)	K_L (L/mmol)	r^2	n	K_f	r^2
25	0.488	0.521	28.369	0.995	2.407162	0.865209	0.889
35	0.502	0.533	42.535	0.997	2.596991	0.95126	0.926
45	0.603	0.634	46.279	0.995	3.094395	0.985737	0.987

reported in Table 2, 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 the resin. The increase in the values of K_L with increasing temperatures refers the increase of the binding strength between the dye and the surface of the resin.

The degree of suitability of the obtained resin towards dyes was estimated from the values of the separation factor (R_L) using the following relation [32].

$$R_L = \frac{1}{1 + K_L C_0} \quad (11)$$

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 resin towards the adsorption of RB5 lie between 0.260 and 0.021 for all concentration ranges at 25 °C. This implies that the adsorption of RB5 on GMA/MBA-TEPA resin from aqueous solutions is favorable under the conditions used in this study.

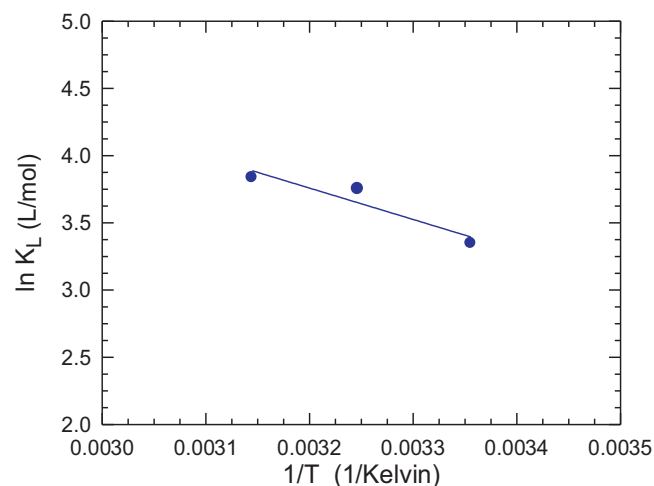
The values of K_L at different temperatures were processed according to the following van't Hoff equation [33] to obtain the thermodynamic parameters of the adsorption process

$$\ln K_L = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (12)$$

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 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. 8 and reported in Table 3. 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 [34]. Gibbs free energy of adsorption (ΔG°) was calculated from the following relation and given in Table 3

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (13)$$

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 [35]. 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 resin towards RB5 at higher temperature. The data given in Table 3 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

**Fig. 8.** van't Hoff plots for the uptake of RB5 anions onto GMA/MBA-TEPA.

adsorption process is dominated by entropic rather than enthalpic changes [35].

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 (2, 4 and 8 mL/min) and a fixed bed height of 1.1 cm are shown in Fig. 9, 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 behavior 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 4. As shown in Fig. 10, the bed height was varied from 1.1 to 4.4 cm while the flow rate was held constant at 8 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 resin 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

Table 3
Enthalpy, entropy and free energy change for adsorption of RB5 anions on the studied resin at different temperatures.

Temperature (K)	ΔH° (kJ/mol)	ΔS° (J/molK)	ΔG° (kJ/mol)	$T\Delta S^\circ$ (kJ/mol)
298			-8.41	27.81
308	19.40	93.34	-9.34	28.74
318			-10.28	29.68

Table 4
Data of column studies for the uptake of RB5 anions at different bed heights and flow rates.

Bed height (cm)	Flow rate (mL/min)	t_s (h)	t_b (h)	$Q_{\max, \text{exp}}$ (mmol/g)	K_a (L/mmol h)	N_0 (mmol/L)	Z_0 (cm)	r^2
1.1	2	23.25	0.75	0.439				
1.1	4	13	0.40	0.417				
1.1	8	7.25	0.20	0.385				
2.2	8	11.75	0.4	0.400	15.3	120	0.764	0.999
4.4	8	20.25	0.8	0.424				

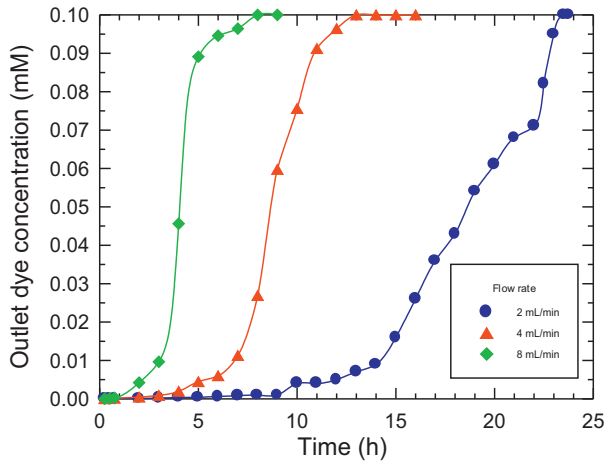


Fig. 9. Effect of flow rate on breakthrough curves for the adsorption of RB5 anions by GMA/MBA-TEPA from initial concentration of 0.1×10^{-3} M and pH 3.

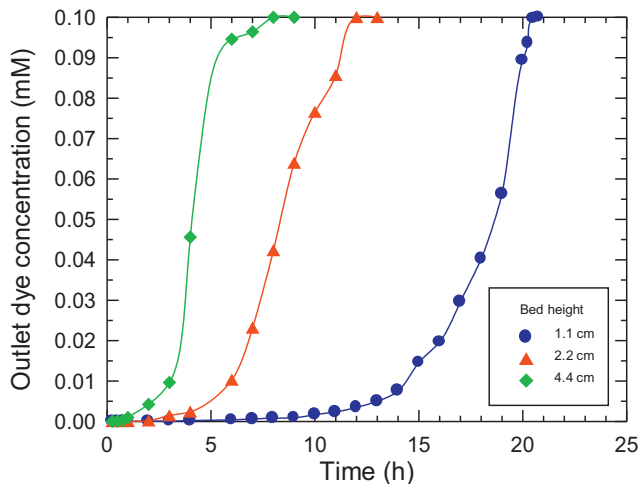


Fig. 10. Effect of bed height on breakthrough curves for the adsorption of RB5 anions by GMA/MBA-TEPA from initial concentration of 0.1×10^{-3} M and pH 3.

the following equation [36].

$$t_s = \frac{N_0 Z}{C_0 v} - \frac{1}{K_a C_0} \ln \left(\frac{C_0}{C_t} - 1 \right) \quad (14)$$

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 were calculated from the slope and intercept of the BDST plots (Fig. 11), 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 value of K_a for GMA/MBA-TEPA resin is 15.3 (L/mmol h), respectively. Again the obtained K_a value of the studied resin is consistent with

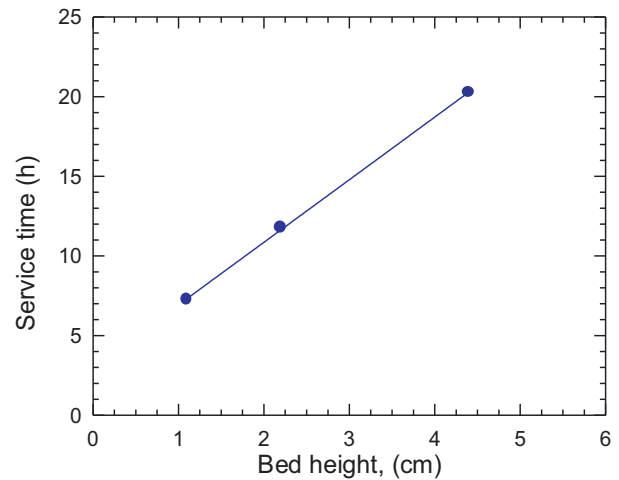


Fig. 11. Bed depth service time model for the adsorption of RB5 anions by GMA/MBA-TEPA from initial concentration of 0.1×10^{-3} M and pH 3.

its long breakthrough time (12–48 min). The critical bed height (Z_0) can be calculated by setting $t_s = 0$ in Eq. (13) [34].

$$Z_0 = \frac{v}{K_a N_0} \ln \left(\frac{C_0}{C_b} - 1 \right) \quad (15)$$

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 [36]. The critical bed height for GMA/MBA-TEPA resin column was calculated as 0.764 cm.

3.3.3. Resin regeneration

Fig. 10 shows the desorption of RB5 anions from resin GMA/MBA-TEPA resin using 0.1 M, 0.5 M and 1.0 M NaOH as eluent. As shown in Fig. 12 the highest RB5 concentration was detected in the effluent in the first 10 mL of both 0.5 and 1.0 M NaOH then the concentration of RB5 gradually decreased until zero concentration after flowing 50 mL of both concentrations. While in case of using 0.1 M NaOH as eluent the concentrations of RB5 decreased to nearly its half value compared with both 0.5 and 1.0 M NaOH solutions and the zero concentration of RB5 was reached after flowing 110 mL of the eluent. The desorption ratio was calculated using the following equation:

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

The desorption ratios $\approx 96.7\%$, 98.0% and 98.8% for 0.1 and 0.5 and 1.0 M NaOH, respectively.

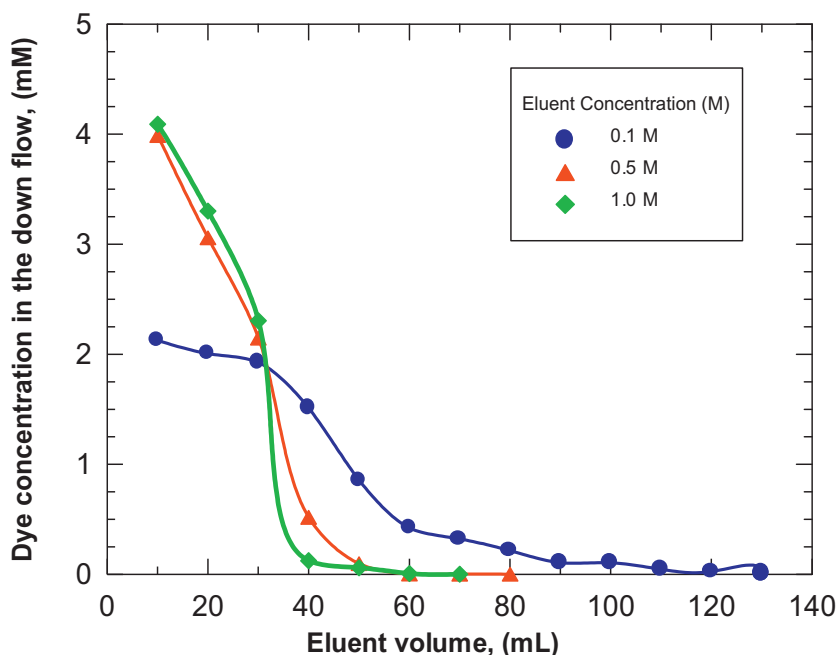


Fig. 12. Elution of RB5 anions from GMA/MBA-TEPA using different concentrations of NaOH.

4. Conclusions

Removal of RB5 anions from aqueous solutions was studied using GMA/MBA-TEPA resin. The prepared resin was characterized via estimating the concentration of amino groups, water regain, surface area and zeta potential measurements. The amine active sites determined was found to be 4.6 mmol/g. The surface area was calculated to be 90 m²/g. Water regain value are (24 ± 3%), which reflects the hydrophilic character of the prepared resin. The nature of interaction between the anions and the resin was found to be dependent upon the acidity of the medium. The sorption process carries out by anion exchange mechanism. The removal process was carried out through batch and column methods. Kinetic studies referred that the adsorption reaction follows pseudo-second order model. Thermodynamic parameters obtained indicated that the adsorption process is an endothermic spontaneous reaction and proceeds according to Langmuir isotherm. The maximum uptake value was found to be 0.603 mmol/g at 45 °C. The breakthrough curves of the studied resin towards adsorption of RB5 were investigated at different flow rates and bed heights. The studied resin showed long t_s (780–1395 min) and t_b (12–48 min) during the adsorption of RB5 onto a mini-column of GMA/MBA-TEPA resin. The critical bed height for the studied column was calculated as 0.764 cm at flow rate of 8 mL/min, which indicates a promising applicability of the studied resin for the complete removal of RB5 from aqueous media. Elution experiments were performed using different concentrations of NaOH. The resin was regenerated effectively using 0.5 M NaOH.

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