

Application of the commercial anion exchange membrane for adsorptive removal of Eriochrome Black-T from aqueous solution

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ABSTRACT

This work reported batch adsorption of Eriochrome Black-T (EBT) from aqueous solution at room temperature onto the commercial anion exchange membrane (AEM) epoxypropyltrimethylammonium chloride (EPTAC). The influence of contact time, membrane dosage (amount of adsorbent), initial concentration dye solution, temperature, ionic strength and pH on adsorption capacity was investigated in detail. Adsorption isotherms including Langmuir, Freundlich, Dubinin–Radushkevich and Temkin were utilized to explore experimental results for adsorption of EBT from aqueous solution onto the commercial anion exchange membrane EPTAC. Adsorption kinetics study demonstrated that EBT adsorption onto the commercial anion exchange membrane EPTAC fitted to pseudo-second-order kinetic model. Adsorption thermodynamics investigations showed that EBT adsorption onto the commercial anion exchange membrane EPTAC was exothermic process ($\Delta H^\circ = -34.82$ kJ/mol). Moreover, the value of mean free energy ($E = 38.46$ kJ/mol) from Dubinin–Radushkevich isotherm and standard enthalpy ($\Delta H = -34.82$ kJ/mol) showed that EBT adsorption onto the commercial anion exchange membrane EPTAC was chemical adsorption process. Hence, it can be employed as an outstanding candidate for EBT removal at room temperature from aqueous solution.

Keywords: Adsorption isotherms; Exothermic process; Commercial anion exchange membrane EPTAC; Adsorption; Eriochrome Black-T

1. Introduction

Synthetic dyes were especially utilized for paper printing, textile dyeing, leather dyeing, color photography and in petroleum product as additives [1]. Due to their significance including excellent color fastness, bright colors, and

luxury uses, reactive dyes are the most usually utilized dyes [2,3]. On the other hand, the digestible colors have always been utilized in food or drink products and are called as 'food dyes', 'food additives' or 'edible dyes' [4]. Different chemical structures were exhibited by them. Heterocyclic groups and substituted aromatic were responsible for it.

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Several reactive dyes that are linked by an azo groups are azo compounds [5]. Several reactive dyes were virulent to some organisms and they originated direct eradication of water's creature [6]. Artificial food colorings have been in the controversy for several years and scrutinized for being possibly linked to cancer, allergies and hyperactivity [4]. Further, the solubility of reactive dyes into water is high. Hence, their removal from sewage is progressive by ordinary biological treatment and physico-chemical procedures [7,8].

Many conventional procedures for the discharge of dyes from wastewater include physical, chemical and biological processes. They include adsorption [9], coagulation [10], oxidation [11], reduction [12], filtration [13], and biological treatment [14]. Adsorption and biological treatment are two crucial procedures employed for wastewater treatment. The biological treatment is hard to start up and control [15] and intermediate product (aromatic amines) produced during anaerobic reduction of azo dyes are known to be potential carcinogens [16]. Adsorption on the other hand, should be a favourable method because of economical feasibility, simplicity of design, recycling of adsorbent, applicability of wide variety of adsorbate, no pre-treatment requirements, and non-extence of harmful residues [17,18]. In literature, the adsorbents studied included natural or synthetic products such as zeolites, activated clay, activated carbons, bio-nano-composite (Alg-Cst/Kal), Curcuma caesia based activated carbon, Ag doped MnO₂-CNT nano-composite bimetallic-carbon nano-composite, activated slag, chitosan beads, cellulosic resins, polymeric resin, modified rice husk, modified cross-linked starch, palm kernel fiber, red mud, bottom ash, de-oiled soya, plant leaves, etc. [19–43]. From one adsorbent to other, the price and efficiency vary significantly.

Currently, outstanding adsorption capacity and established efficient alteration property for the recovery and removal of reactive dyes was exhibited by the commercial anion exchange resins [19,44]. Because the particle form of the anion exchange resins, their packed-bed operations would endure from specific flaws. The anion exchange membranes were used to overcome problems for the removal of anionic reactive dyes Cibacron blue 3GA and Cibacron red 3BA from water instead of resin particles [45]. It can not only overcome technical problems of packed-bed operation but also show the property of simple scale-up by simple stacking many membranes together or employing a large membrane area. Therefore, the ion exchange membrane become good selection as adsorbent for industrial uses.

In our previous work, we used the commercial anion exchange membrane (AEM) epoxypropyltrimethylammonium chloride (EPTAC) for the adsorptive removal of different anionic dyes from aqueous solution [46–48]. This work reports application of the commercial anion exchange membrane EPTAC for the adsorptive removal of Eriochrome Black-T (EBT) from aqueous solution. The effect of operating factors including contact time, amount of adsorbent (the commercial membrane EPTAC dosage), temperature, pH and initial concentration of EBT in an aqueous solution and ionic strength on adsorption capacity of the commercial anion exchange membrane (AEM) EPTAC was studied in detail. Adsorption equilibrium, kinetics, and thermodynamics for

EBT adsorption onto the commercial anion exchange membrane EPTAC was also investigated.

2. Experimental

2.1. Adsorbent

The Chemjoy Membrane Co., Ltd., Hefei, Anhui, China kindly supplied the commercial anion exchange membrane EPTAC. It was used for the adsorptive removal of EBT from an aqueous solution. It exhibited ion exchange capacity (IEC) of 0.42 mmol/g and water uptake (W_R) of 164.31% [46,47].

2.2. Adsorbate

Herein, Eriochrome Black-T (EBT) was employed as adsorbate. Its molecular formula is C₂₀H₁₂N₃NaO₇S and has molecular weight of 461.38 g/mol. The entire chemicals were used as received. Deionized water was utilized through this research. Its chemical structure is shown in Fig. 1.

2.3. Adsorption test

In this manuscript, batch adsorption of EBT onto the commercial anion exchange membrane EPTAC at room temperature was performed as described in our previous work [46,47]. Firstly, we prepared EBT aqueous solution by dissolving its measured quantity at room temperature into distilled water. The optimized contact time was determined by shaking the calculated mass of the commercial anion exchange membrane EPTAC (0.1 g) into 40 mL of EBT aqueous solution with initial concentration of 50 mg/L for different time intervals such as 30, 60, 90, 120, 180, 240, 360, 600, 900 and 1,440 min at constant shaking speed of 120 rpm. To calculate the optimized mass of the commercial anion exchange membrane EPTAC, the varying amounts of the commercial anion exchange membrane EPTAC such as 0.02, 0.04, 0.06, 0.08, and 0.10 were shaken into 40 mL of EBT aqueous solution with initial concentration of 50 mg/L for

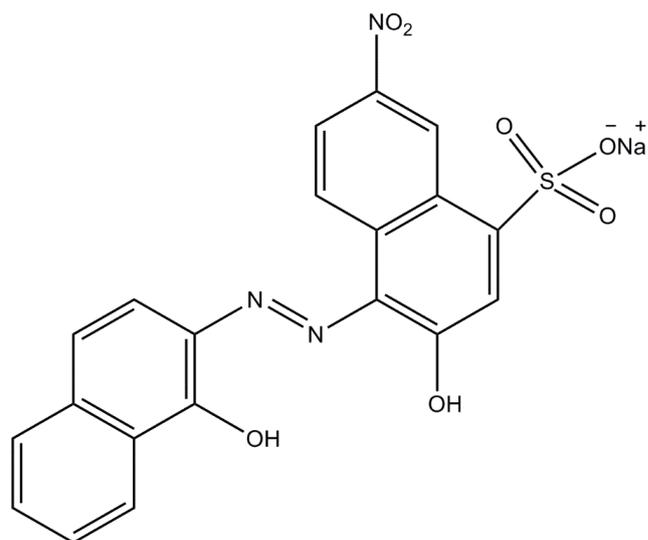


Fig. 1. Molecular structure of Eriochrome Black-T.

1,440 min at constant shaking speed of 120 rpm. To explore adsorption isotherms, the measured amount of the commercial anion exchange membrane EPTAC (0.10 g) was shaken at speed of 120 rpm for 1,440 min into 40 mL of EBT aqueous solution with initial concentration of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 200, 300, 400, 500, and 1,000 mg/L. Adsorption thermodynamics for EBT adsorption onto the commercial anion exchange membrane EPTAC was studied by shaking its measured quantity (0.10 g) into 40 mL of EBT aqueous solution with initial concentration of 50 mg/L at 293, 303, 313, 323 and 333 K for 1,440 min at shaking speed of 120 rpm. To study effect of ionic strength on EBT adsorption, different concentration of NaCl was added into EBT aqueous solution to attain different molarities such as 0.2, 0.5, 1.0 and 1.5 M. Then, the measured amount of the commercial anion exchange membrane EPTAC (0.1) was shaken into 40 mL of EBT aqueous solution with initial concentration of 50 mg/L having different molarities such as 0.2, 0.5, 1.0 and 1.5 M at shaking speed of 120 rpm for 1,440 min at room temperature. To investigate the effect pH on EBT adsorption onto the commercial anion exchange EPTAC, the pH of EBT aqueous solution was changed from 2 to 11. The concentration of EBT was calculated by determining the absorbance of the supernatant at wavelength ($\lambda_{\max} = 530$ nm for EBT) by using UV/VIS spectrophotometer (UV-2550, SHIMADZU). The concentration of EBT was determined by employing calibration curve. Adsorption capacity was determined by using below equation:

$$q_t = \frac{C_o - C_t}{W} \times V \quad (1)$$

where C_o (mg/L) and C_t (mg/L) indicate concentration of EBT at initial state and at time t respectively. Similarly V (L) shows volume of EBT aqueous solution and W (g) denotes the mass of the commercial anion exchange membrane EPTAC respectively.

2.4. Adsorption equilibrium

Adsorption isotherms including Langmuir isotherm, Freundlich isotherm, Dubinin–Radushkevich isotherm and Temkin isotherm were used to explain EBT adsorption onto the commercial anion exchange membrane EPTAC. Their details are as follows:

2.4.1. Langmuir isotherm

It is based on the maximum adsorption corresponds to the saturated monolayer of liquid molecules on the solid surface. It is given as follows [49].

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad (2)$$

where K_L is Langmuir constant (L/mg) and Q_m is Langmuir monolayers adsorption capacity (mg/g), C_e is supernatant concentration at equilibrium state of the system (mg/L), and q_e is the amount of dye adsorbed at equilibrium state of system (mg/g). The essential characteristics of Langmuir isotherm can be shown in term of dimensionless constant separation factor R_L that is given by [50].

$$R_L = \frac{1}{1 + K_L C_o} \quad (3)$$

The value of R_L shows the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [51]

2.4.2. Freundlich isotherm

It is an empirical relation utilized to explain the heterogeneous system. The Freundlich isotherm model is expressed as [52].

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where K_f and n_f are Freundlich constant.

2.4.3. Dubinin–Radushkevich isotherm

The Dubinin–Radushkevich model is represented as [37]

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (5)$$

where β (mol²/kJ) is constant related to the adsorption energy and ε is the Polanyi potential can be calculated by employing below equation:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (6)$$

where R is gas constant (8.31 kJ/mol) and T is absolute temperature (K). The mean free energy E (kJ/mol) can be determined by below relationship.

$$E = \frac{1}{\sqrt{2\beta}} \quad (7)$$

2.4.4. Temkin isotherm

The linear form of Temkin isotherm is represented as [37]:

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (8)$$

where $B_T = RT/b_T$, R is gas constant (8.31 J/mol K) and T is absolute temperature (K). The constant b_T is related to the heat of adsorption and A_T is equilibrium binding constant coinciding to the maximum binding energy.

2.5. Adsorption kinetics

Several kinetic models including pseudo-first-order model, pseudo-second-order model, Elovich model, liquid-film diffusion model, modified Freundlich equation and Bangham equation were employed to study kinetics for EBT adsorption onto the commercial anion exchange membrane EPTAC. Their details are as follows:

2.5.1. Pseudo-first-order model

The Lagergren pseudo-first-order rate in linear form is shown as [38,39,53]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (9)$$

where k_1 (min^{-1}), q_e (mg/g) and q_t (mg/g) are rate constant of pseudo-first-order model, concentration of EBT adsorbed at equilibrium and time t respectively.

2.5.2. Pseudo-second-order model

The pseudo-second-order kinetic model in linearized form is expressed as [36,54–56]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

where k_2 (g/mg min) is the rate constant of pseudo-second-order model.

2.5.3. Elovich model

The Elovich model is represented as [47,57]:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (11)$$

where α (mg/g min) and β (g/mg) are constants. The parameter α is initial adsorption rate and β is the extent of surface coverage and activation energy for chemisorption.

2.5.4. Liquid-film diffusion model

It is shown as:

$$\ln(1 - F) = -K_{fd} t \quad (12)$$

where K_{fd} is liquid-film diffusion rate constant, and $F = q_t/q_e$.

2.5.5. Modified Freundlich equation

It was developed by Kuo and Lotse [58,59]

$$q_t = k C_o t^{1/m} \quad (13)$$

where k , C_o , t and m represented adsorption rate constant (L/g min), initial concentration (mg/L), contact time (min) and the Kuo-Lotse constant respectively. Its linear form is expressed as:

$$\ln q_t = \ln(k C_o) + \frac{1}{m} \ln t \quad (14)$$

2.5.6. Bangham equation

Bangham equation is represented as [58,59]

$$\log\left(\frac{C_o}{C_o - q_t m}\right) = \log\left(\frac{k_o m}{2.303 V}\right) + \alpha \log t \quad (15)$$

where m is weight of the commercial anion exchange membrane EPTAC utilized (g/L), V is volume of dye solution (mL), α (<1) and k_o ($\text{mL}/(\text{g/L})$) are constants.

2.6. Adsorption thermodynamics study

Adsorption thermodynamics for EBT adsorption onto the commercial anion exchange membrane EPTAC was explored by calculating the change in Gibb's free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) by using following equations:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (16)$$

$$K_c = \frac{C_a}{C_e} \quad (17)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (18)$$

where ΔG° , K_c , R , ΔH° and ΔS° represented change in Gibb's free energy (kJ/mol), equilibrium constant, general gas constant, change in enthalpy (kJ/mol) and change in entropy (J/mol K) respectively.

3. Results and discussion

3.1. Effect of operating factors

The influence of operating factors including contact time, mass of adsorbent (the commercial anion exchange membrane EPTAC dosage), initial concentration of EBT in an aqueous solution, temperature, ionic strength and pH on adsorption capacity was described as:

3.1.1. Effect of contact time

Fig. 2a represents the effect of contact time on adsorption capacity of the commercial anion exchange membrane EPTAC for batch EBT adsorption at room temperature from an aqueous solution. It was explored by keeping shaking speed (120 rpm), concentration of adsorbate (50 mg/L), and amount of adsorbent constant at room temperature. It was found to be increased 8.10 to 19.10 mg/g with increase in contact time which is similar to our previous work [60]. Table 1 shows an interesting comparison of EBT adsorption capacity of the commercial anion exchange membrane EPTAC with different adsorbents reported in literature. It got saturation after 24 h. It showed that EBT adsorption onto the commercial anion exchange membrane EPTAC attained equilibrium within 24 h and this optimum contact time was employed for further study. It showed that EBT adsorption was fast in the initial stage due to higher number of available vacant sites on the surface of adsorbent (the commercial anion exchange membrane EPTAC) during the initial stage.

3.1.2. Effect of membrane dosage

The effect membrane dosage on adsorption capacity of the commercial anion exchange membrane EPTAC for EBT was studied by keeping other operating parameters such as contact time, initial dye concentration, shaking speed and temperature constant and results are represented in Fig. 2b. Results showed that adsorption capacity was

found be decreased from 50.80 to 19.10 mg/g with increasing the membrane dosage. It was due to increase in the number of available active position with enhancing the membrane dosage from 0.02 to 0.10 g. Similar results were previously reported in literature [57,60,61]. However, it was not observed any significant change in adsorption capacity with further enhancement in the membrane

dosage and it could be due to the saturation of binding sites [62].

3.1.3. Effect of initial dye concentration

Fig. 2c depicts the effect of initial concentration of EBT aqueous solution on adsorption capacity of the commercial

Table 1
Comparison of adsorption capacity of the commercial anion exchange membranes EPTAC for EBT with different adsorbents

Adsorbents	Adsorption capacity (mg/g)	References
Commercial anion exchange membrane	19.10	This work
Hydrophobic cross-linked polyzwitterionic acid	15.90	[65]
Untreated almond shell	6.06	[66]
Cold plasma treated almond shell	18.18	[66]
β -Cyclodextrins/polyurethane foam material	20.17	[67]
<i>Litchi chinensis</i>	7.0	[68]
Alginate/basil seed mucilage biocomposite	9.52	[69]
Eucalyptus bark	52.37	[70]
Diatom-xerogel (DXC)	47.01	[71]
Epibromohydrin modified	42.30	[72]
Bottom ash	108	[73]

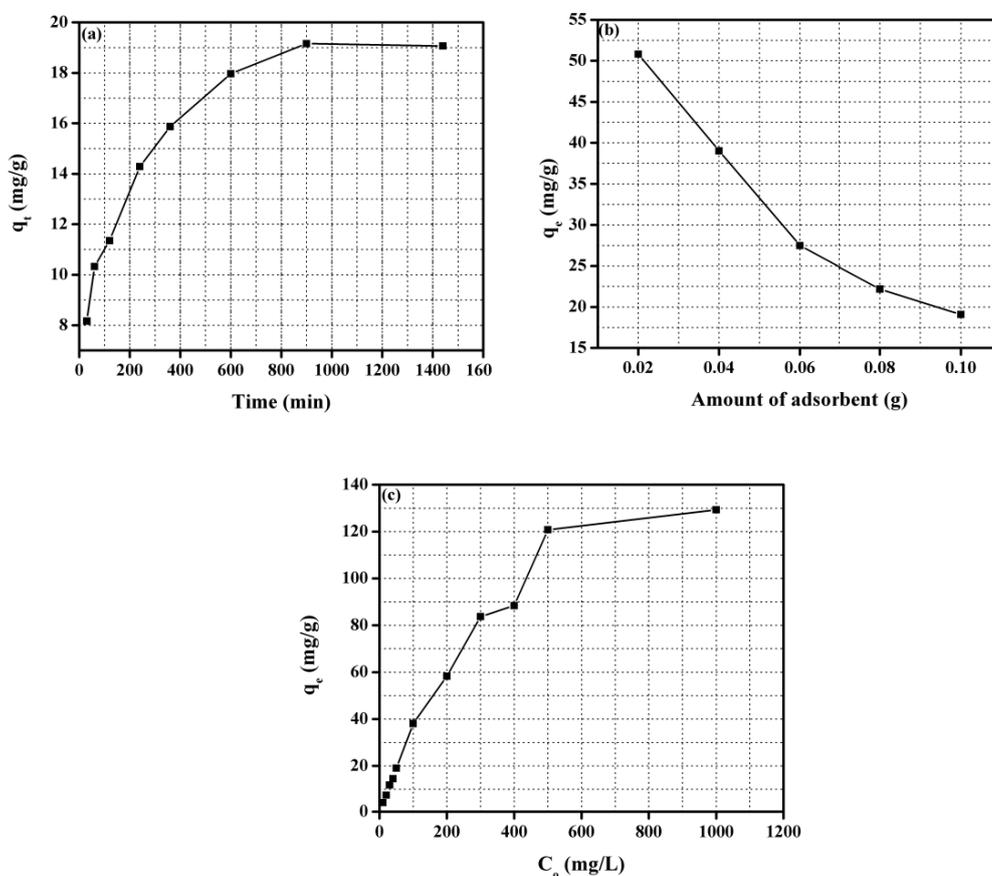


Fig. 2. (a) Effect of contact time, (b) membrane dosage, and (c) initial concentration of dye on adsorption capacity of the commercial anion exchange membrane EPTAC.

anion exchange membrane EPTAC. It was conducted by keeping other operating factors including contact time, membrane dosage, shaking speed and temperature constant. Results represented that adsorption capacity was found to be enhanced from 3.50 to 130 mg/g with increasing initial concentration of EBT aqueous solution from 10 to 1,000 mg/L. The initial dye concentration provided useful driving force to overcome the resistance of mass transfer from the aqueous phase to the solid phase [63]. It enhanced the interaction between EBT and the commercial anion exchange membrane EPTAC. Therefore, adsorption capability of the commercial anion exchange membrane EPTAC for EBT was increased.

3.1.4. Effect of temperature

Fig. 3a depicts the influence of temperature on adsorption capacity of the commercial anion exchange membrane EPTAC for EBT. It was investigated by keeping contact time, membrane dosage, initial concentration of dye, and shaking speed constant. Adsorption capacity was found to be decreased from 19.10 to 15.60 mg/g with rise in temperature. It is because of decline in surface activity with rise in temperature [54,59]. Hence, adsorption of EBT onto the commercial anion exchange membrane EPTAC was exothermic process.

3.1.5. Effect of ionic strength

It is a significant factor that control both electrostatic and non-electrostatic interactions between dye and the membranes surface. The effect of ionic strength on adsorption capacity of the commercial anion exchange membrane EPTAC for EBT from an aqueous solution was studied by addition of different amount of sodium chloride into dye solution and attained results are shown in Fig. 3b. It was noted that adsorption capacity was found to be decreased with increasing the concentration of salt. Adsorption capacity of dye was decreased from 17 to 15.68 mg/g with increasing the concentration of salt from 0.2 to 1.5 M. It showed that the employed commercial anion exchange membrane EPTAC was convenient and tolerable to the water with higher concentration of salt. This could be due to the competition between the EBT anions and Cl^- for the active adsorption sites [64].

3.1.6. Effect of pH

Fig. 3c depicts the effect of pH on adsorption capacity of the commercial anion exchange membrane EPTAC for EBT. Herein, the pH of the dye solution was changed from 2 to 11. As EBT is diprotic dye. Based on different pH, it is dissociated. Only one proton was dissociated at lower pH value

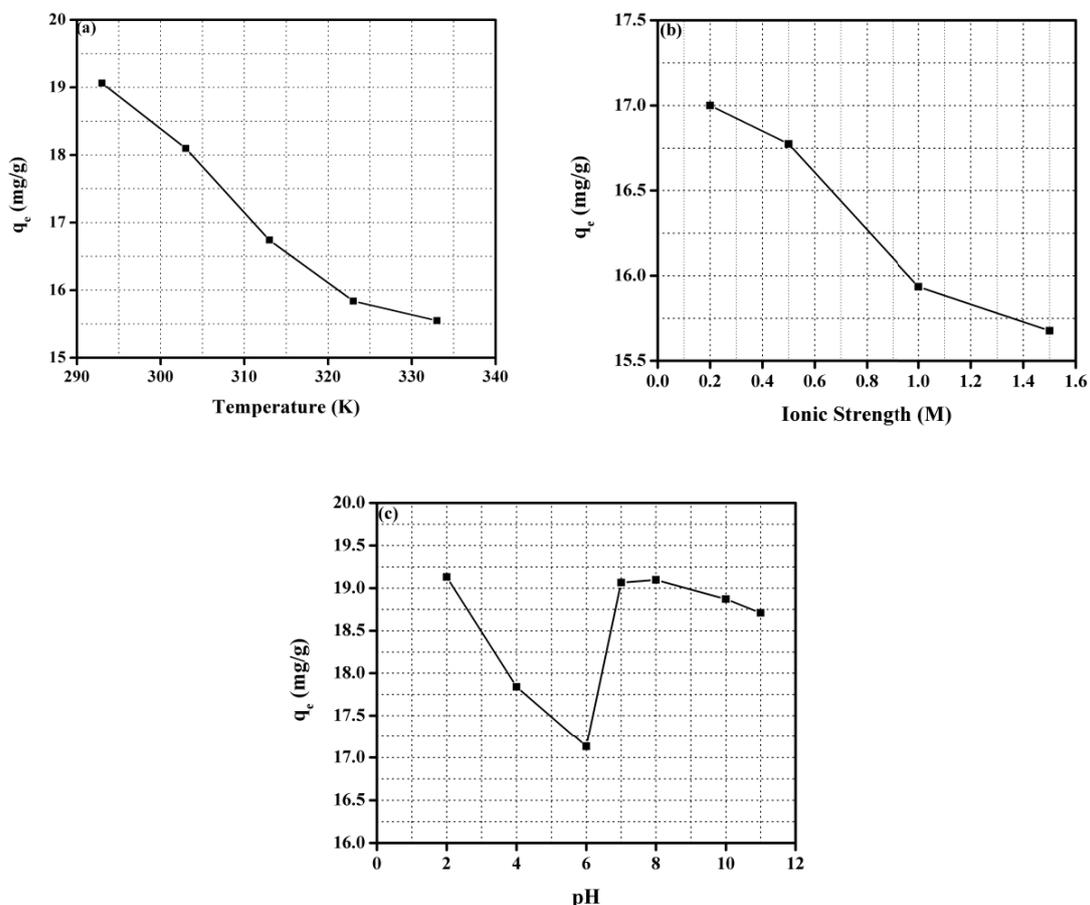


Fig. 3. (a) Effect of temperature, (b) ionic strength, and (c) effect of pH on adsorption capacity of EBT.

which resulted to small negative charge on dye molecules. At lower pH (acidic pH), the ammonium group (cationic head group) of the commercial anion exchange membrane EPTAC was protonated. Due to this, it attracted the anionic dye EBT in the aqueous solution because of electrostatic force of attraction. From Fig. 3c, it was noted that the value of adsorption capacity was found to be lower at pH = 6 due to dissociation of both protons of dye which resulted strong repulsion between EBT and the commercial anion exchange membrane EPTAC. The increase in pH higher than 7 has not resulted to significant increase in adsorption capacity of the commercial anion exchange membrane EPTAC for dye. Therefore, the maximum adsorption capacity was noted at pH (neutral) of 7. Therefore, all study was conducted at neutral pH of EBT aqueous solution.

3.2. Adsorption isotherms

Herein, experimental data for EBT adsorption onto the commercial anion exchange membrane EPTAC was subjected to several isotherm models including Langmuir, Freundlich, Dubinin–Radushkevich and Temkin. Langmuir isotherm for EBT adsorption onto the commercial anion exchange membrane EPTAC is shown in Fig. 4a and the

measured values of its parameters are represented in Table 2. It was noted that the value of determined coefficient ($R^2 = 0.995$) was close to unity. It exhibited that EBT adsorption onto the commercial anion exchange membrane EPTAC fitted well to Langmuir isotherm. Moreover, the calculated value of R_L (0.019–0.160) exhibited that EBT adsorption onto the commercial anion exchange membrane EPTAC was favorable process. Fig. 4b depicts Freundlich isotherm for EBT adsorption onto the commercial anion exchange membrane EPTAC. The determined values of its factors are given in Table 2. From here, it was found that the value of correlation coefficient ($R^2 = 0.961$) was close to unity represented that EBT adsorption onto the commercial anion exchange membrane EPTAC followed Freundlich isotherm. The Freundlich constant ' n ' value ranges from 2–10 exhibiting good adsorption, 1–2 indicated moderate adsorption and less than one denoted poor adsorption [53,74]. Fig. 4c represents Dubinin–Radushkevich isotherm for EBT adsorption onto the commercial anion exchange membrane EPTAC and the determined values of Dubinin–Radushkevich constant (Q_m and β) are given in Table 2. The calculated value of mean adsorption energy ($E = 38.46$ kJ/mol) for EBT adsorption onto the commercial anion exchange membrane EPTAC showed that it was chemical

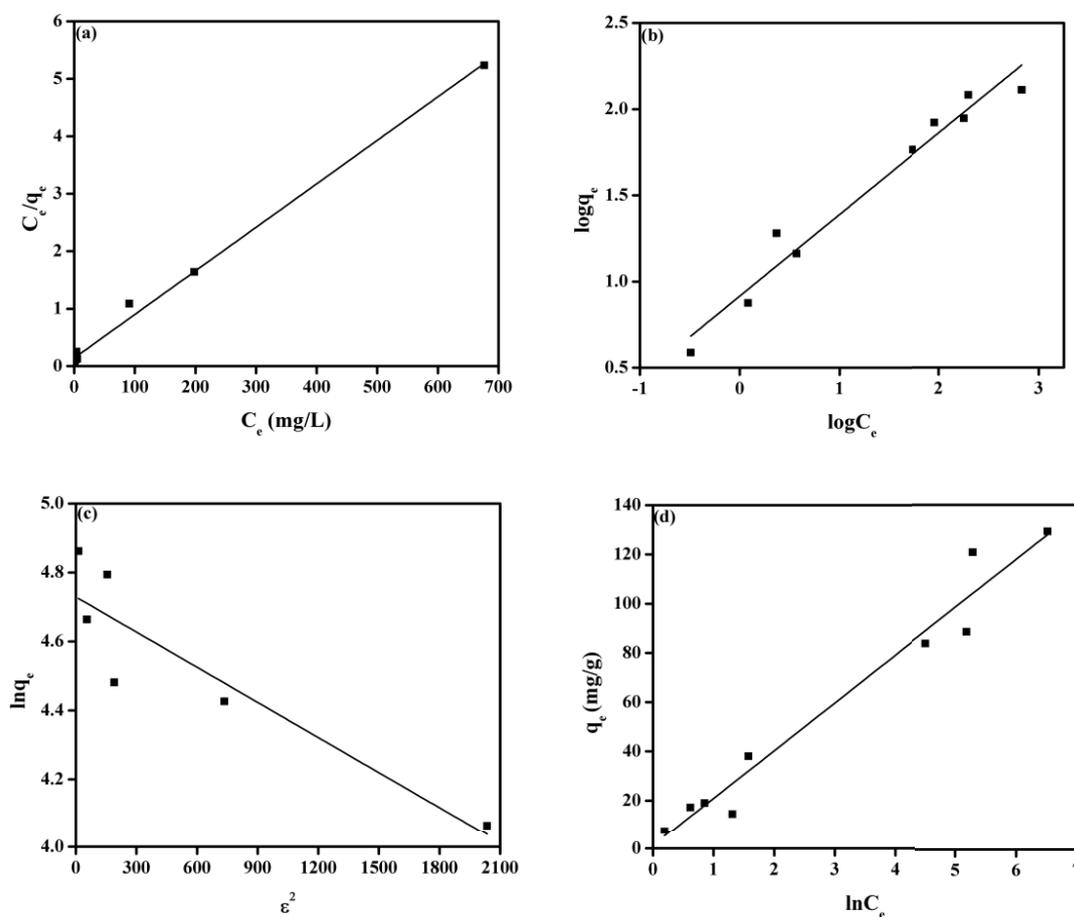


Fig. 4. (a) Langmuir, (b) Freundlich, (c) Dubinin–Radushkevich, and (d) Temkin isotherms for EBT adsorption onto the commercial anion exchange membrane EPTAC.

Table 2
Determined values of adsorption isotherms parameter for EBT adsorption onto the commercial anion exchange membrane EPTAC [Q_m (mol/g); K_L (L/mol); K_f ((mg/g)(L/mg)^{1/n}); C_m (mol/g); β (mol²/J²); E (kJ/mol)]

Adsorption isotherm models	Determined parameters	
Langmuir isotherm	Q_m	133.33
	$K_L \times 10^{-2}$	5.22
	R_L	0.019–0.160
	R^2	0.995
	n	2.11
Freundlich isotherm	K_f	8.24
	R^2	0.961
	β	3.40×10^{-4}
Dubinin–Radushkevich isotherm	Q_m	113.30
	R^2	0.789
	E	38.46
	b_T	127.78
Temkin isotherm	A_T	1.08
	R^2	0.957

adsorption process. Moreover, the Temkin isotherm for EBT adsorption onto the commercial anion exchange membrane EPTAC is depicted in Fig. 4d and the determined values of b_T and A_T are given Table 2. The value of correlation coefficient ($R^2 = 0.957$) was lower than Langmuir isotherm denoting that EBT adsorption onto the commercial anion exchange membrane EPTAC was not fitted to Temkin isotherm.

3.3. Adsorption kinetics

Herein, adsorption kinetics for EBT adsorption was studied by utilizing several kinetic models. Fig. 5a denotes the plot of $\log(q_e - q_t)$ vs. time for EBT adsorption onto the commercial anion exchange membrane EPTAC and the determined value k_1 from slope is given in Table 3. Herein, the correlation coefficient (R^2) value for EBT adsorption was 0.972. It has been observed that there was a large difference between experimental adsorption capacity ($q_{e,exp} = 19.10$ mg/g) and calculated adsorption capacity values ($q_{e,cal} = 9.46$ mg/g), therefore the rate process can not be explained by pseudo-first-order model. The pseudo-second-order model is represented in Fig. 5b and the determined value of adsorption capacity (q_e) and k_2 are given Table 3. It was noted that the values of calculated

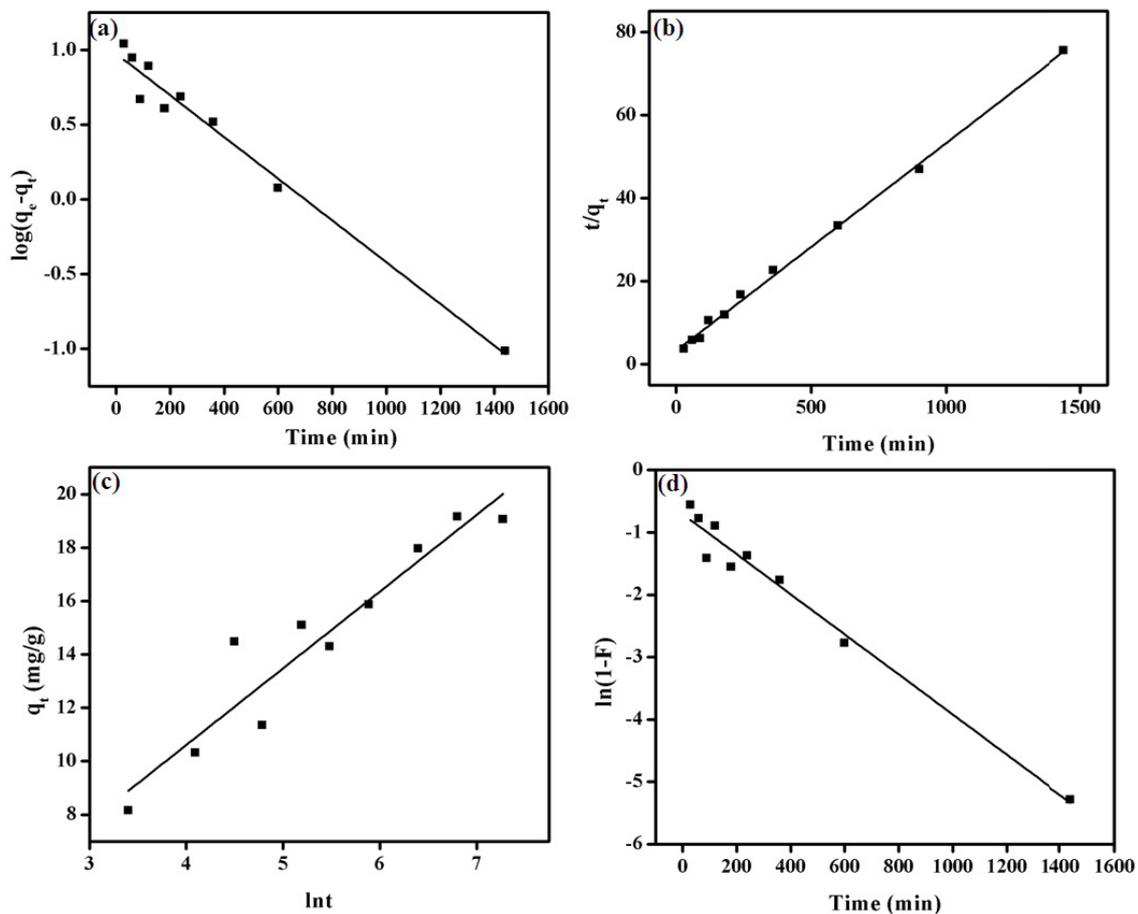


Fig. 5. (a) Pseudo-first-order model, (b) pseudo-second-order model, (c) Elovich model, and (d) liquid-film diffusion model for EBT adsorption onto the commercial anion exchange membrane EPTAC.

adsorption capacity (19.99 mg/g) and experimental value (19.10 mg/g) were very close to each other. Moreover, the value of correlation coefficient ($R^2 > 0.99$) was close to unity. These results showed that EBT adsorption onto the commercial anion exchange membrane EPTAC fitted well to the pseudo-second-order model. The Elovich model for EBT adsorption is depicted in Fig. 5c. The measured values of α and β for EBT adsorption are given in Table 3. It was observed that the values of correlation coefficient ($R^2 = 0.892$) for Elovich model was less than pseudo-second-order model. The liquid film model for EBT adsorption is shown in Fig. 5d and the measured value of K_{fd} is given in Table 3. Results represented that liquid-film diffusion model is not suitable to explain EBT adsorption because the value of correlation coefficient ($R^2 = 0.972$) was lower than pseudo-second-order model.

Fig. 6a denotes modified Freundlich model and the determined values of m and k from slope and intercept are given in Table 3. The value of correlation coefficient ($R^2 = 0.850$) was lower than pseudo-second-order model. The plot of Bangham equation is shown in Fig. 6b and the calculated values of α and m from slope and intercept are given in Table 3. The diffusion of adsorbate (EBT) into pores of adsorbent (commercial anion exchange membrane EPTAC) is not the only rate controlling step because the double logarithmic plot did not give linear curves for this model [75,76]. For EBT adsorption from aqueous solution, it may be that both film and pore diffusion were significant to different extent.

3.4. Adsorption thermodynamics

To evaluate adsorption thermodynamics for EBT adsorption onto the commercial anion exchange membrane EPTAC, we determined Gibb's free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) and the attained values of are shown in Table 4. The negative value of enthalpy ($\Delta H^\circ = -34.82$ kJ/mol) represented that EBT adsorption onto

the commercial anion exchange membrane EPTAC was an exothermic process while the negative value of entropy ($\Delta S^\circ = -95.73$ J/mol) represented the decline in randomness at the adsorbate–adsorbent interface during the adsorption of EBT onto the commercial anion exchange membrane EPTAC. From Table 4, it was noted that the values of Gibb's free energy (ΔG°) was positive at all temperature investigated and increased from 15.17 to 17.24 kJ/mol with rise in temperature. It was associated to the intraction between adsorbent and adsorbate, with unbalanced competition imputed to heterogeneity of membrane surface and system attained energy at higher temperatures from outer source [47].

Table 3
Determined values of kinetic parameters for EBT adsorption onto the commercial anion exchange membrane EPTAC (q_e : mg/g; k_1 : (min⁻¹); k_2 : g/mg min; α : mg/g min; β : g/mg; K_{fd} : (min⁻¹); k : L/g min; k_o : mL/g/L)

Adsorption kinetic models	Determined parameters		
Pseudo-first-order model	$q_{e,exp}$	19.10	
	q_e	$k_1 \times 10^{-3}$	R^2
Pseudo-second-order model	9.46	1.4	0.972
	q_e	$k_2 \times 10^{-4}$	R^2
Elovich model	19.99	7.7	0.997
	α	β	R^2
Liquid-film diffusion model	2.12	0.35	0.892
	$K_{fd} \times 10^{-3}$	C_{fd}	R^2
Modified Freundlich equation	3.2	-0.71	0.972
	m	k	R^2
Bangham equation	4.76	0.091	0.850
	k_o	α	R^2
	3.7	0.21	0.851

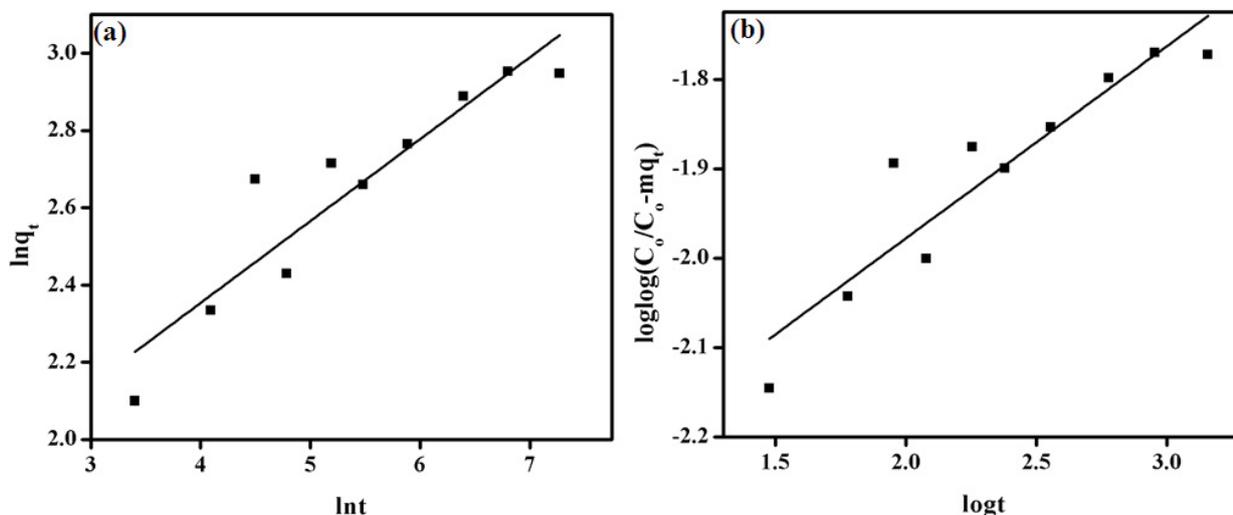


Fig. 6. (a) Modified Freundlich equation and (b) Bangham equation for EBT adsorption onto the commercial anion exchange membrane EPTAC.

Table 4

Calculated values of thermodynamic parameters for EBT adsorption onto the commercial anion exchange membrane EPTAC

ΔH (kJ/mol)	ΔS (J/mol)	ΔG (kJ/mol)				
		293 K	303 K	313 K	323 K	333 K
-34.82	-95.73	15.17	15.69	16.21	16.24	17.24

4. Conclusions

In summary, batch adsorption of EBT from an aqueous solution at room temperature onto the commercial anion exchange membrane EPTAC was studied. Results represented that adsorption capacity was enhanced with increasing contact time, membrane dosage, initial concentration of EBT aqueous solution while declined with temperature and ionic strength. Moreover, adsorption capacity of the commercial anion exchange membrane EPTAC for EBT was also influenced by changing pH of dye solution. Adsorption isotherms study showed that EBT adsorption onto the commercial anion exchange membrane EPTAC fitted well to Langmuir isotherm model. Results of kinetic study showed that EBT adsorption onto the commercial anion exchange membrane EPTAC fitted well to pseudo-second-order model. Adsorption thermodynamic study exhibited that EBT adsorption onto the commercial anion exchange membrane EPTAC was exothermic process. From here, it was concluded that the commercial anion exchange membrane EPTAC could be utilized as extraordinary adsorbent for EBT adsorption from an aqueous solution.

Symbols

AEM	—	Anion exchange membrane
A_T	—	Equilibrium binding constant coinciding to the maximum binding energy, L/mg
b_T	—	heat of adsorption, J/mol
b	—	Langmuir constant, L/mg
C_o	—	Initial Concentration of dye, mg/L
C_t	—	Concentration of dye at time t , mg/L
EBT	—	Eriochrome Black-T
EPTAC	—	Epoxypropyltrimethylammonium chloride
ΔG°	—	Change in Gibb's energy
ΔH°	—	Change in enthalpy
IEC	—	Ion exchange capacity, mmol/g
K_f	—	Freundlich constant
k_1	—	Rate constant of pseudo-first-order model, min^{-1}
k_2	—	Rate constant of pseudo-second-order model, g/mg min
K_{fd}	—	Liquid-film diffusion rate constant
k	—	Apparent adsorption rate constant, L/g min
W	—	Weight of adsorbent, g
V	—	Volume of adsorbate, dm^3
α	—	Initial sorption rate, mg/g min
β	—	Extent of surface coverage and activation energy for the chemisorption, g/mg
m	—	Kuo-Lotse constant.
Q_m	—	Langmuir monolayer adsorption capacity, mg/g
R	—	Gas constant, 8.31 J/mol K

ΔS°	—	Change in entropy
T	—	Absolute temperature, K
W_R	—	Water uptake, %

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