Removal of different anionic dyes from aqueous solution by anion exchange membrane

Muhammad Ali Khan[1,2], Muhammad Imran Khan[*3] and Shagufta Zafar[4]

[1]*Key Laboratory of Optoelectronic Materials chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of sciences, Fuzhou, Fujian 350002, P.R. China*
[2]*University of Chinese Academy of Sciences, Beijing 100039, P.R. China*
[3]*CAS Key Laboratory of Soft Matter Chemistry, Lab of Functional Membranes, School of Chemistry and Material Science, University of Science and Technology of China, Hefei, Anhui 230026, P.R China*
[4]*Department of Chemistry, The Govt. Sadiq College Women University, Bahawalpur 63000, Pakistan*

Abstract. Adsorption is a widely used technique for the removal of dyes from wastewaters by variety of adsorbents. In this work, the main focus is on the potential assessment of anion exchange membrane for the removal of different dyes using batch system and investigation of experimental data by applying various kinetic and thermodynamic models. The removal of anionic dyes i.e., Eosin-*B*, Eriochrome Black-*T* and Congo Red by anion exchange membrane BII from aqueous solution was carried out and effect of various parameters such as contact time, membrane dosage, temperature and ionic strength on the percentage removal of anionic dyes was studied. The experimental data was assessed by kinetic models namely pseudo-first-order, pseudo-second-order, Elovich liquid film diffusion, Bangham and the modified Freundlich models equation have been used to analyze the experimental data. These results indicate that the adsorption of these anionic dyes on BII follows pseudo-second-order kinetics with maximum values of regression coefficient (0.992-0.998) for all the systems. The adsorption of dyes was more suitable to be controlled by a liquid film diffusion mechanism. The adsorptive removal of dye Eosin-B and Eriochrome Black-*T* were decreased with temperature and thermodynamic parameters such as free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) for adsorption of dyes on membrane BII were calculated at 298 K, 308 K and 318 K. The values of enthalpy and entropy were negative for EB and EBT representing that the adsorption of these dyes on BII is physiosorptive and exothermic in nature. Whereas the positive values of enthalpy and entropy for CR adsorption on BII, indicating that its adsorption is endothermic and spontaneous in nature. It is evident from this study that anion exchange membrane has shown good potential for the removal of dyes from aqueous solution and it can be used as adsorbent for dues removal on commercial levels.

Keywords: adsorption; anion exchange membrane; anionic dyes; Kinetics; thermodynamics

1. Introduction

Dyes are widely used in various industries such as textile, paper, plastic, cosmetics and leather,

---

∗Corresponding author, Ph.D., E-mail: emran@mail.ustc.edu.cn

for coloring their final products (Alireza Nezamzadeh-Ejhieh and Mahshid Khorsandi 2010, Lin *et al.* 2008). It is known that public perception of water is highly effected by the color, which has been recognized as the first contaminant in wastewater (Crini 2006). The presence of small amount of dye in water (less than 1 ppm for some dyes) is highly visible and undesirable (Robinson *et al.* 2001). Once the dye contaminated the water, its removal by conventional wastewater treatment method is particularly difficult because many dyes are stable to light and oxidizing agents and resistant to aerobic bio-oxidation. There are many methods for dye removal such as biological treatment (Allegre *et al.* 2006, Pala and Tokat 2002, Kapdan and Kargi 2002), coagulation (Gupta *et al.* 2006, Cooper 1993), chemical oxidation, and photo catalytic processes (Liu and Chiou 2006, Clark *et al.* 1994, Solozhenko *et al.* 1995), ozone treatment (Allegre *et al.* 2006, Cooper 1993), membrane processes (Cooper 1993, Buckley 1992, Jiraratananon *et al.* 2000, Koyuncu 2002, Allegre *et al.* 2006, Treffry-Goatley *et al.* 1983) and adsorption (Cooper 1993, Karcher *et al.* 2001, Netpradit *et al.* 2003, Allegre *et al.* 2006, Gupta *et al.* 1997, Gupta *et al.* 2004, Gupta *et al.* 2005, Gupta *et al.* 2006). The adsorption technology for in situ treatment of polluted considered as a potential method to eliminate the color from wastewater streams due to its easy handling, fast operational readiness, low discharge generation and low operational costs having high reversibility of the removal process. Several researchers have used the adsorption process to remove the color compounds with ion-exchange resins which are important examples of synthetic adsorbents for wastewater treatment (Ganna *et al.* 2016, Silvia *et al.* 2017, Namasivayam *et al.* 1994). The adsorption of large molecules (such as dyes) needs an adsorbent with major mesoporous fractions to increase the efficiency of the process (Pelekani and Snoeyink 1999, Lorenc-Grabowska and Gryglewicz 2007). The adsorbents tested in the literature included natural or synthetic products such as zeolites, activated clays, activated carbons, activated slag, chitosan beads, cellulosic resin, polymer resin, modified rice husk, modified cross-linked starch, palm kernel fiber, red mud, bottom ash, ion exchangers and granulated ferric hydroxide (Karcher *et al.* 2001, Gupta *et al.* 1997, Gupta *et al.* 2004, Gupta *et al.* 2005, Gupta *et al.* 2006, Namasivayam *et al.* 1994, Pelekani and Snoeyink 1999, Lorenc-Grabowska and Gryglewicz 2007, Liu *et al.* 2007). Their price and efficiency change from one adsorbent to another.

In comparison to several commercial adsorbents, anion exchange resins were evaluated as an effective adsorbent for removal of reactive dyes (Karcher *et al.* 2001, 2002). Ion exchange resins have porous morphology and have some problems in their packed-bed operations, e.g. slow pore diffusion, flow channeling, low accessible flow rate, high pressure drop and non-uniform packing. These problems can be minimized by using ion exchange membranes, i.e., the membrane shape of ion exchange resins. The microporous membrane system not only removes the technical diadvantages of packed-bed operations but also shows the characteristics of simple scale-up by simple stacking more membranes together or employing a larger membrane area. This idea has been verified successfully in the previous research (Liu *et al.* 2007, Lin *et al.* 2008, Khan *et al.* 2015a, Khan *et al.* 2016a) that adopted commercial polymeric ion-exchange membrane to remove anionic reactive dyes and cationic reactive dyes from water.   It makes ion-exchange membrane a useful adsorbent for dye removal from wastewater.

In the present work, the removal of anionic dyes namely Eosin-*B*, Erichrome Black-*T* and Congo Red from aqueous solution by commercial anion exhange membrane BII is studied. The effect of parameters such as contact time, membrane dosage, temperature and ionic strength on the removal of these dyes has been investigated. Adsorption kinetics is studied by using pseudo-first-order model, pseudo-second-order model, Elovich model, liquid film diffusion model, the Bangham equation and the modified Freundlich equation. Thermodynamic study is also

conducted for adsorption of these dyes onto anion exchange membrane BII.

2. Experimental material and Method

2.1 Materials

2.1.1 Adsorbent

The commercial anion exchange membrane BII provided by Chemjoy Membrane Co. Ltd, Hefei, Anhui, China was used as adsorbent. It was prepared from blends of PVA and QPPO. It was used without further treatment. The ion exchange capacity (IEC) and water uptake (WR) of anion exchange membrane BII are 0.38 mmol/g and 41.6% repectively.

2.1.2 Adsorbate

Three commercial anionic dyes namely Eosin *B*, Eriochrome Black-*T* and Congo Red obtained from Fluka chemicals were used as adsorbates. The stock solution of 1000 mg/L was prepared by dissolving 1.0 g of accurately weighed dye into 1 litre of deionized water and required concentrations were obtained by further dilution of stock solution. All the chemicals used in the experiments were of analytical reagent grade. The properties of anionic dyes used are given in Table 1. The structures of these dyes are shown in Fig. 1.
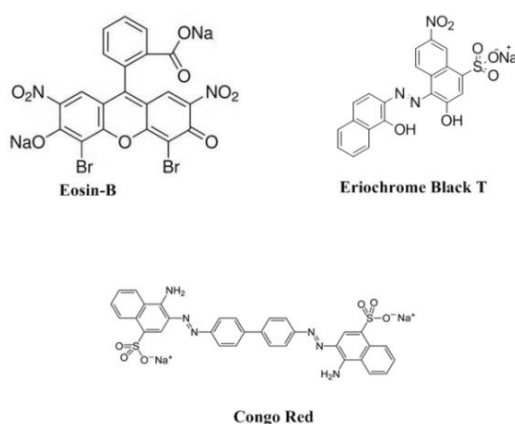

Fig. 1 Molecular structure of Eosin-*B*, Eriochrome Black *T* and Congo Red dye

Table 1 The properties on anionic dyes

Characteristics	Eosin-B	Eriochrome Black T	Congo Red
CAS number	548-24-3	1787-61-7	573-58-0
Molecular Formula	$C_{20}H_8Br_2N_2O_9$	$C_{20}H_{12}N_3O_7SNa$	$C_{32}H_{22}N_6Na_2O_6S_2$
Molecular weight (g/mol)	624.08	461.38	496.66
Groups	carboxlic and anthracene -O⁻	Sulphonic	Sulphonic
Number of anionic groups	2	1	2
λ_{max} (nm)	514	530	490

2.2 Adsorption

Batch adsorption experiments were carried out by immersing anion exchange membrane BII into the measured volume of all anionic dyes aqueous solutions with a shaking speed of 75 rpm at room temperature. The concentrations of these dyes were measured by UV/VIS spectrophotometer (UV-2550, SHIMADZU) and related caliberation curves were obtained. The wavelengths of 514 nm, 530 nm 464 nm were set for Eosin-*B*, Erichrom black-*T* and Congo Red respectively. The effect of membrane dosage on the removal of these anionic dyes from aqueous solution was studied by changing the amount of adsorbent keeping the other parameters such as contact time of 48 hours, initial dyes concentration of 50 mg/L and solution volume of 40 mL and shaking rate of 75 rmp constant at room temperature.

The amount of dyes adsorbed onto the anion exchange membrane at time "*t*", q_t (mg/g) was measured by the following relation

$$q_t = \frac{C_o - C_t}{W} \times V \tag{1}$$

where C_o and C_t are the concentrations of dyes at initial state and at time *t* respectively. Similarly *V* and *W* are volume of dyes aqueous solution and weight of anion exchange membrane respectively.

2.3 Characterization

2.3.1 FTIR analysis

FTIR analysis of anion exchange membrane BII was recorded by attenuated total reflectance (ATR) with FTIR spectrometer (Vector 22, Bruker) in the range of 4000-400 cm^{-1}.

2.3.2 Morphology

The morphology of anion exchange membrane BII was studied by employing Field emission scanning electron microscope (FE-SEM, Sirion200, FEI Company, USA).
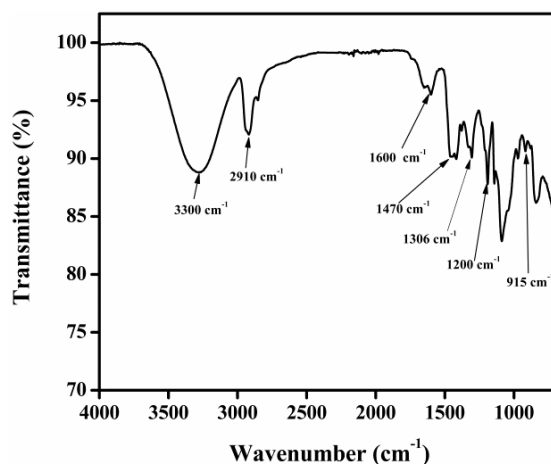

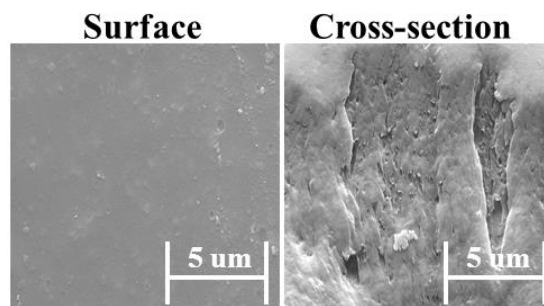Fig. 2(a) FTIR spectra of anion exchange membrane BII

Fig. 2(b) SEM image of surface (Left) and cross-section (Right) anion exchange membrane BII

3. Results and discussion

3.1 Characterization

3.1.1 FTIR analysis

Fig. 2(a) represented the FTIR spectra of anion exchange membrane BII. The characteristic peak appeared at 3300 cm^{-1} is attributed to the stretching vibration of -OH group in the anion exchange membrane BII. The characteristic band at 915 cm^{-1} in the spectra of BII is associated to the C-N stretching vibration (Khan *et al*. 2016b). The adsorption peaks of symmetrical and asymmetrical stretching vibration of C-O are at 1200 cm^{-1} and 1306 cm^{-1} and those of phenyl group at 1469 cm^{-1} and 1604 cm^{-1} respectively (Khan *et al*. 2017, Khan *et al*. 2106c, Khan *et al*. 2016d). The peak in the region of 2850-2985 cm^{-1} in the spectra of BII is corresponding to -CH3 stretching vibration from PPO backbone (Khan *et al*. 2015b).

3.1.2 Morphology

The morphology of anion exchange membrane BII was studied by scanning electron microscopy (SEM). Fig. 2(b) depicted the surface and cross-section images of anion exchange membrane BII used in the present wok. It can be seen that the used AEM possess uniform and dense morphology. There is no visible pore, hole or crack on the membrane surface.

3.2 Effect of contact time

The effect of contact time on the removal efficiency of anion exchange membrane for these anionic dyes from aqueous solution was investiged keeping the initial dye concentration of 50 mg/L, solution volume of 40 ml, shaking rate of 75 rmp and   membrane dosage of 0.1 g constant at room temperature and results are shown in Fig. 3(a). It is clear that the adsorption of all these dyes was rapid in the start because the large number of empty sites on anion exchange membrane were present for adsorption of dyes and after that it became slower. The maximum removal of these anionic dyes attains after 48 hours. Thus, the equilibrium contact time for these anoinic dyes is 48 hours and after that removal of dyes is almost constant. The contact time is one of the most important parameter for economical wastewater treatment applications (Kadirvelu *et al*. 2005). Therefore, it is suggested that the contact time of 48 hour is required to attain better removal of these anionic dyes from aqueous solution using anion exchange membrane BII as a adsorbent. The removal of anionic dyes EB and CR were higher than EBT due to their different properties and
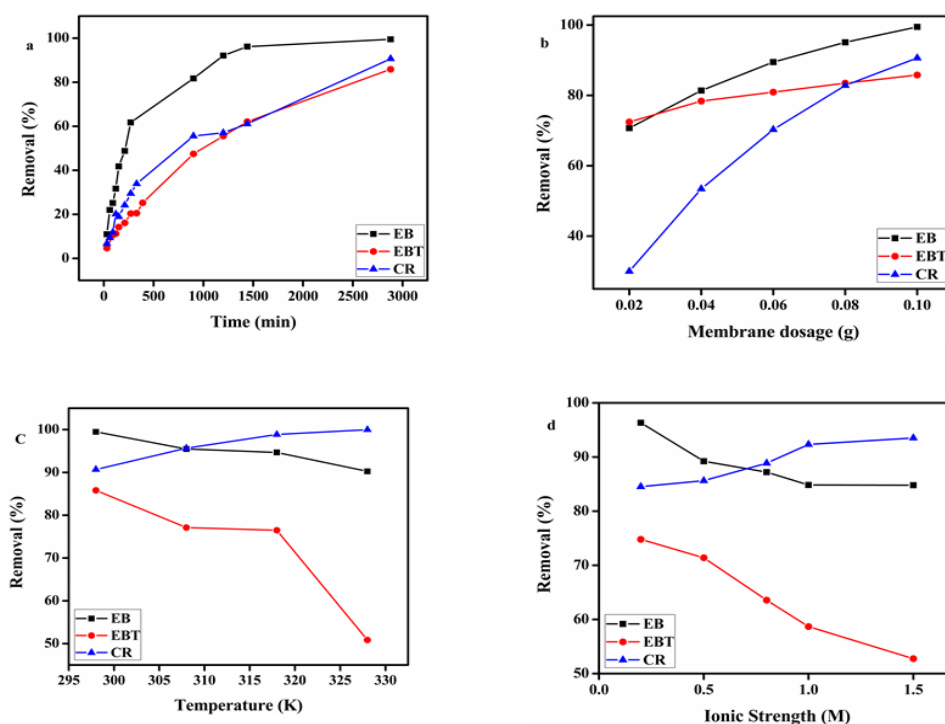
Fig. 3 Effect of operational parameters on adsorption of EB, EBT and CR dyes on anion exchange membrane BII (a) effect of contact time; (b) effect of membrane dosage; (c) effect of temperature; (d) effect of ionic strength

structures. The anionic dye EB have carboxlic and anthracene groups that can be attached with two ion exchange groups thus making strong bond with anion exchange membrane (adsorbent) leading to higher adsorption. Similarly, anionic dye CR have two sulphonic groups that can be bonded with two ion exchange groups thus making strong bond with adsorbent. Moreover, amino groups present in the CR are electron donating which facilitates the interaction of sulphonic groups with ion exchnge membrane resulting in higher removal of dye. On the other hand, EBT have only one sulphonic group which is also sterically hindered. Further, nitro group (NO_2) attached with it is electron withdrawing thus deactivating the interaction between EBT and ion exchange membrane leading to lower adsorption of EBT.

3.3 Effect of membrane dosage

It is clear that the removal of anionic dyes increases with increasing the membrane dosage and results are shown in Fig. 3(b). The removal of these anionic dyes Eosin-*B*, Eriochrome Black-*T* and Congo Red was found to be increased from 70.71% to 99.47%, 72.45% to 85.80% and 29.99% to 90.64% respectively with increasing the membrane dosage from 0.02 to 0.1 g. With increasing the membrane dosage, the percentage of removal of anionic dyes increases because the number of available sorption sites on the surface of anion exchange membrane increases. There is no significant change in the percentage removal after this amount so this dose amount was taken as optimum amount for further experimentation.

3.4 Effect of temperature

The effect of temperature on the percentage removal of these anionic dyes from aqueous solution by anion exchange membrane was investigated. The results were conducted by varing the temperature from 298 K to 328 K keeping the initial dyes concentraion of 50 mg/L, solution volume of 40 ml, membrane dosage dosage of 0.1 g, shaking rate of 75 rmp and contact time of 48 hour constant. The obtained results for removal of these anionic dyes are shown in Fig. 3(c). It is shown that the removal of EB and EBT is found to be decreased from 99.47% to 90.23% and 85.80% to 50.84% respectively by increasing temperature from 298 K to 318 K. These results indicate that removal of EB and EBT onto BII is an exothermic process. The decrease in adsorption with increasing temperature is be due to decrease in surface activity with increasing temperature (Zhang *et al*. 2012). On the other hand, the removal of CR is found to be increased from 90.64% to 99.85% with increasing temperature as shown in Fig. 3(c), indicating that high temperature favors the removal of CR dye from aqueous solution. This increase in adsorption is due to the decrease in solubility of dye with increasing temperature. Further, increase in temperature increases the mobility of large dye ions which may be responsible to increase in adsorption of dye. An increasing number of molecules may acquire sufficient energy to undergo an interaction with active sites at the surface (Dogan and Alkan 2003). Thus, the adsorption of CR increases with temperature which shows that the adsorption of CR is an endothermic process. The enhanced amount of adsorption with the rise in temperature may be either due to acceleration of some originally slow adsorption steps or due to creation of some new active sites on the adsorbent surface.

3.5 Effect of ionic strength

Mostly the wastewater contains different types of dyes and salts. The adsorption was found to be strongly influenced by the concentration and nature of ionic species (Alkan and Dogan 2001). The effect of ionic strength on the percentage removal of these anionic dyes from aqueous solution by anion exchange membrane was studied. It is shown that the removal of EB and EBT dyes on anion exchange membrane decreases with increasing the ionic strength at room temperature as shown in Fig. 3(d) With increasing the concentration of NaCl salt from 0.2 M to 1.5 M, the percentage removal of EB and EBT is found to be decreased from 96.33% to 84.83 % and 74.78% to 52.75% respectively. The negative effect of ionic strength on the adsorption of these dyes is due to competition between the dye anions and Cl- for the active sorption sites (Gong *et al*. 2005). On the other hand, the removal of CR from aqueous solution is not affected with rising the concentration of NaCl from 0.2 M to 1.5 M. This shows that there is no competition between Cl- ions and sulphonate group of CR dye for sorption site on anion exchange membrane. The removal of CR increases with the ionic strength as shown in Fig. 3(d) because the addition of salt enhances the aggregation of dye molecules and decreases the solubility. An increase in aggregation promotes the adsorption of dye molecules (Karadag *et al*. 2007). Another possibility is that the increase in ionic strength enhances the positive charge of the adsorbent surface thus increases the electrostatic attraction between dye (CR) and ion exchange membrane. Thus, the adsorption of CR is found to be increased with increasing the ionic strength. Thus, it is concluded that anion exchange membrane BII can be utilized for removal of CR from water containing salt. The same results were observed for removal of CR by using MgO(III) as adsorbent (Hu *et al*. 2010).
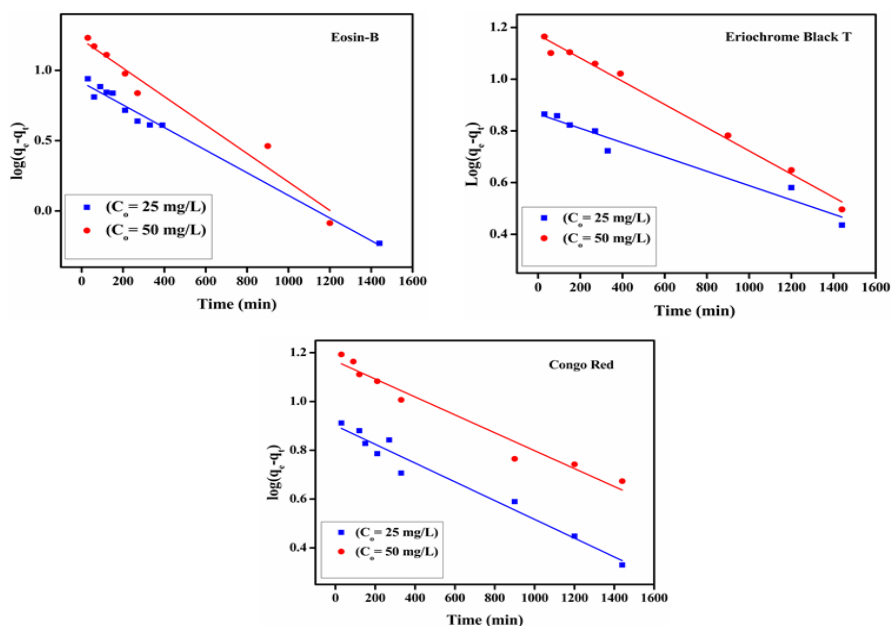
Fig. 4 Pseudo-first order plot for adsorption of EB, EBT and CR dyes on anion exchange membrane BII

3.6 Adsorption kinetics

Many kinetic models are employed to study the controlling mechanism of adsorption reactions such as chemical reaction and diffusion control.

3.6.1 Pseudo-first-order kinetic model

The linearized form of pseudo-first-order rate equation is given by (Bouhamed *et al*. 2012)

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2}$$

where q_e and q_t are the amount of dye adsorbed (mg/g) at equilibrium and time t (min) respectively and k_1 is the rate constant of adsorption (/min). The graphical representation of pseudo-first-order kinetic model for adsorption of anionic dyes onto BII is shown in Fig. 4. The parameters K_1 and q_e for anionic dyes are calculated from slopes and intercepts of plots log(qe-qt) verses t and given in Table 2. The values of correlation coefficients (R^2) for pseudo-first-order kinetics of these anionic dyes with different concentrations are relatively lower. Moreover, there is a large difference between experimental ($q_{e, \exp}$) and calculated ($q_{e, cal}$) adsorption capacity values, representing that the experimental data for these dyes does not fit to pseudo-first-order kinetic model which is similar to the results reported for the adsorption of basic black and anionic reactive dyes onto calcium alginate beads and dirty bentonite (Aravindhan *et al*. 2007, Kheira *et al*. 2016). In fact, in a lot of cases, the Lagergren pseudo-first-order equation could not fit well to the whole range of contact time and is generally applicable over initial stages of the adsorption processes (Ho and McKay 1999, Bulut *et al*. 2008).
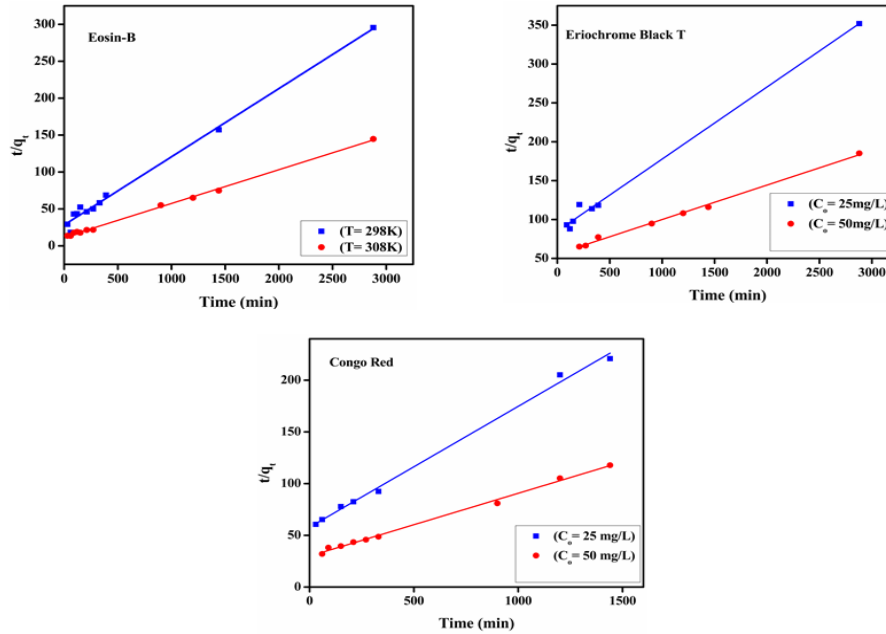
Fig. 5 Pseudo-second order plot for adsorption of EB, EBT and CR dyes on anion exchange membrane BII

3.6.2 Pseudo-second-order kinetic model
The lineaized form of pseudo-second-order kinetics model is expressed as (Ho 2006)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where k_2 (g/mol.min) is second order rate constant. The graphical representation of pseudo-second-order kinetics for adsorption of these anionic dyes onto BII is shown in Fig. 5. The values of q_e and k_2 for these anionic dyes can be determined from the slope and intercept of plots t verses t/q_t and are given Table 2. The values of correlation coefficient (R^2) are close to unity for the all the cases studied. In addition to this, the values of calculated adsorption capacities ($q_{e, cal}$) are in good agreement with the experimental ($q_{e, exp}$) one for the adsorption of these anionic dyes onto BII. These results indicate that adsorption of these dyes onto anion exchange membrane BII followed pseudo-second-order kinetics. Similar kinetics were studied onto LDH-based adsorbents (Benselka-Hadj Abdelkader *et al*. 2011). The values of calculated adsorption capacities (q_e) increases with initial dye concentration for all the cases studied as shown in Table 2. Moreover, the the values of rate constants (k_2) for all these anionic dyes show decline trend due to the the steric hindrance at higher concentraion (Ai *et al*. 2011).

3.6.3 Elovich model
Namasivayam and sangeetha (Namasivayam and Sumithra 2005) indicated that the Elovich expression (Eq. (4)) was initially used to describe the chemosorption kinetics of gases onto solids (Cheung *et al*. 2000). In spites of this, it was widely used and cited in case of chemisorption kinetics of of solid/liquid system (Cortes-Martinez *et al*. 2004). Currently, Elovich equation has been generalized and frequently used in the sorption studies of many pollutants in aqueous
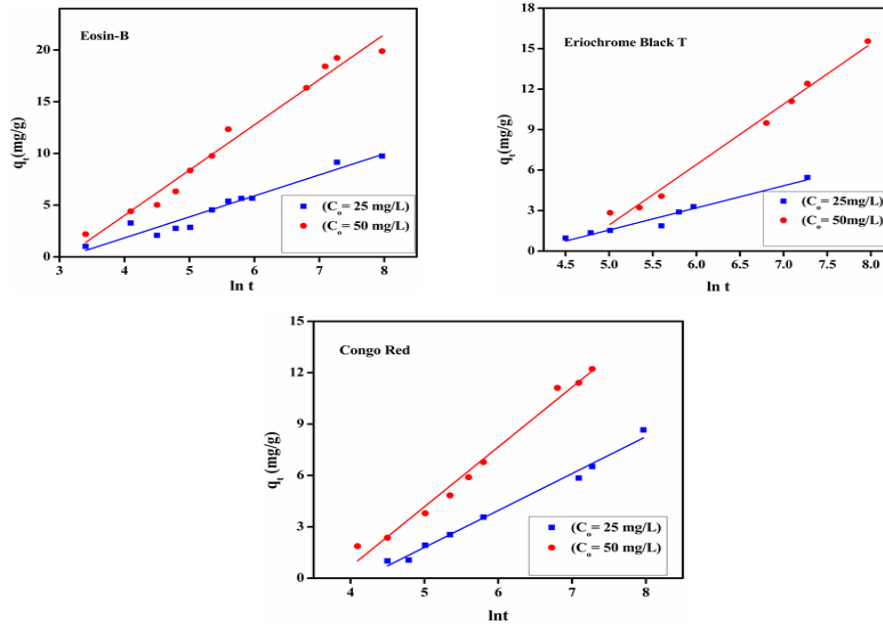
Fig. 6 Elovich model plot for adsorption of EB, EBT and CR on anion exchange membranes BII

solution (Hamdaoui 2006).

$$q_t = \left(\frac{1}{\beta}\right).\ln\left(\alpha.\beta\right) + \left(\frac{1}{\beta}\right).\ln\left(t\right) \tag{4}$$

where α is the chemi-sorption rate (mg/g.min) and β is the desorption constant related to the extent of covered surface and activation energy for chemisorptions (g/mg). The graphical representation of Elovich model for all these dyes with different concentration is shown in Fig. 6. The equation parameters are calculated from slope and intercept of plot of lnt verses q_t and are given in Table 2. The values of both parameters α (mg/g.min) and β (g/mg) changes with varing the initial concentration of dyes. It is observed that the values of β decreases with increasing the concentration of dyes as shown in Table 2 except for the higher concentration. On the other hand the values of α increases with the initial concentration of dyes except for the highest concentration the acid dye. The attained values of correlation coefficient (R^2) for all the dyes with different concentration are lower than pseudo-second order kinetics. As these both kinetic model consider chemisorption of adsorbate with adsorbent molecules it can be concluded that dyes were attached with adsorbent surface by chemical bond in chemical interaction. Elovich equation initially used to show the begining of sorption process, long time before equilibrium, can be used correctly in case of chemisorption with highly heterogeneous materials (Plazinski *et al*. 2009).

3.6.4 Liquid film diffusion model
The liquid film model is expressed as (Chowdhury *et al*. 2011)

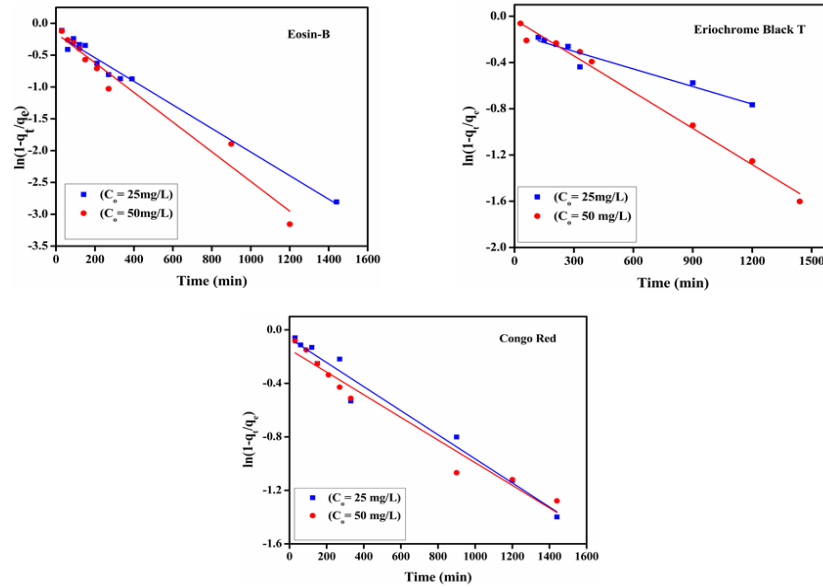$$Ln(1 - \frac{q_t}{q_e}) = -K_{fd}t \tag{5}$$

Fig. 7 Liquid film diffusion model plot adsorption of EB, EBT and CR on anion exchange membranes BII

Fig. 8 Liquid film diffusion model plot adsorption of EB, EBT and CR on anion exchange membranes BII

where K_{fd} is liquid film diffusion rate constant. The plots of $\ln(1-q_t/q_e)$ verses t for liquid film diffusion model for anionic dyes onto anion exchange membrane are shwon in Fig. 7. The values of correlation coefficient (R^2) of these dyes are in arrange of 0.98-0.95 as shown in Table 2. The lines show deviation from the origin in the plot for liquid film diffusion model showing that not only the liquid film mechanism but some other mechanisms were also operative in the adsorption of dyes by anion membranes.

Fig. 9 The Modified Freundlich plot for adsorption of EB, EBT and CR on anion exchange membranes BII

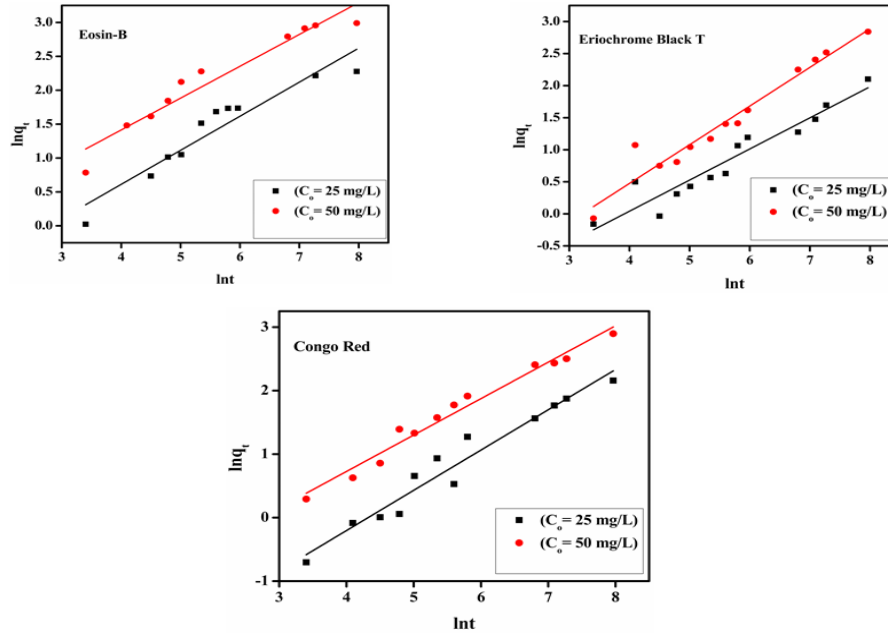### 3.6.5 The Bangham equation

The Bangham equation (Aharoni and Ungarish (1977)) is given as

$$\log \log\left(\frac{C_o}{C_o - q_t m}\right) = \log\left(\frac{k_o m}{2.303V}\right) + \alpha \log t \tag{6}$$

where C_o is the initial concentration of dye solution (mg/L), V is volume of solution (mL), q_t is amount of dye adsorbed (mg/g) at time t, m is weight of adsorbent used (g/L). α (<1) and k_o (mL/(g/L)) are constants. The plot of loglog(C_o/C_o-q_tm) vs logt for all these dyes is given in Fig. 8. The values of α and m are calculated from slope and intercept of Fig. 8 and are given in Table 2. The double logarithmic plot did not give linear curves for all these dyes removal by anion exchange membrane BII indicating that the diffusion of adsorbate into pores of the adsorbent is not the only rate controling step (Tutem *et al*. 1998, Mall *et al*. 2005).

3.6.6 The modified Freundlich equation

The modified Freundlich eaquation was orignally developed by Kuo and Lotse (1973)

$$q_t = kC_o t^{1/m} \tag{7}$$

where q_t amount of adsorbed dye (mg/g) at time t, k apparent adsorption rate constant (L/g.min), C_o the initial dye concentration (mg/L), t the contact time (min) and m is the Kuo-Lotse constant. The values of k and m were used to evaluate the effect of dye surface loading and ionic strength on the adsorption process.

Linear form of modified Freundlich equation is given as

Table 2 Kinetic parameters for adsorption of EB, EBT and CR on anion exchange membrane BII

System	EB		EBT		CR	
	25 mg/L	50 mg/L	25 mg/L	50 mg/L	25 mg/L	50 mg/L
q_e (exp.) (mg/g)	9.74	19.89	8.18	17.16	8.18	17.16
Pseudo-first-order model						
q_e (mg/g)	8.23	16.53	7.33	14.83	7.96	14.62
k_1 (x 10^{-3} /min)	0.80	1.0	0.27	0.45	0.38	0.36
R^2	0.982	0.931	0.952	0.989	0.963	0.959
Pseudo-second-order model						
q_e (mg/g)	10.83	21.88	10.97	22.56	8.15	16.45
k_2 (x10^{-3} g/mg.min)	0.30	0.18	0.10	0.04	2.01	2.03
R^2	0.992	0.998	0.993	0.995	0.995	0.995
Elovich model						
α (x10^{-2}mg/g.min)	0.89	20.4	2.90	4.70	3.30	7.70
β (g/mg)	0.49	0.22	0.61	0.22	0.47	0.29
R^2	0.935	0.976	0.952	0.987	0.986	0.983
Liquid film diffusion model						
k_{fd} ×10^{-3}	1.85	2.33	0.61	1.04	0.90	0.85
C	-0.17	-0.15	-0.15	-0.03	-0.06	-0.14
R^2	0.982	0.963	0.928	0.986	0.970	0.959
The Bangham equation						
k_o (mL/(g/L)	0.51	0.52	0.24	0.11	0.10	0.16
α	0.46	0.47	0.49	0.61	0.64	0.58
R^2	0.844	0.908	0.909	0.947	0.948	0.973
The Modified Freunlich equation						
M	2.16	2.13	2.06	1.65	1.67	1.60
k (×10^{-2}L/g.min)	1.33	1.28	0.60	0.29	0.28	0.40
R^2	0.886	0.926	0.909	0.946	0.948	0.973

$$\ln q_t = \ln\left(kC_o\right) + \frac{1}{m}\ln t \tag{8}$$

The graphical representation of modified Freundlich model for these anionic dyes removal is given in Fig. 9. The parameters m and k are calculated from slope and intercept of Fig. 9 and are given in Table 2. A comparison of k values shows that EB is removed more effectively than EBT and CR by anion exchange membrane BII.

3.6.7 Adsorption thermodynamics

The thermodynamic parameters namely Gibb's free energy (ΔG^o, kJ/mol), enthalpy (ΔH^o, kJ/mol) and entropy (ΔS^o, J/mol.K) changes associated with the adsorption of these anionic dyes onto anion exchange membrane were calculated by employing Gibb's free energy (Eq. (12)) and
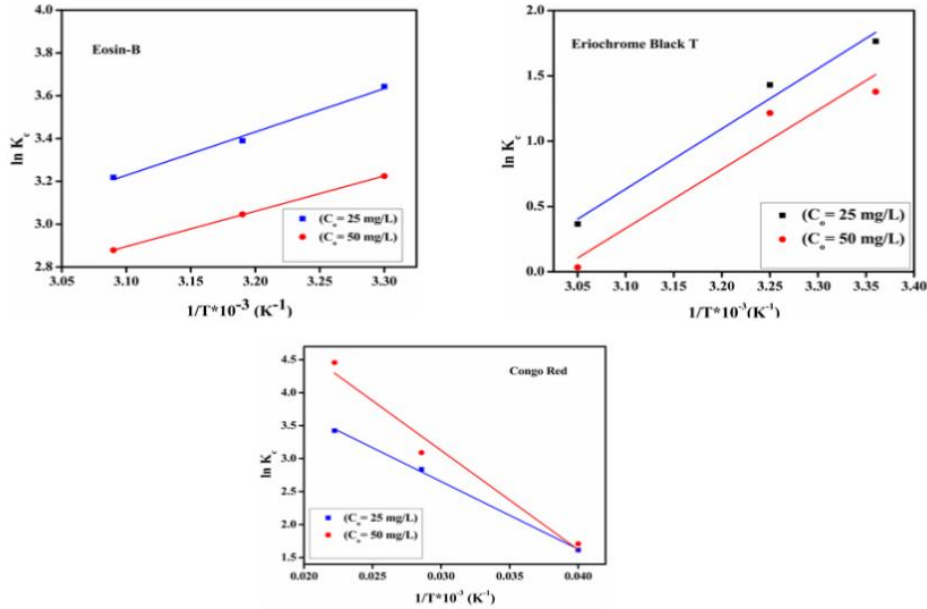
Fig. 10 The Modified Freundlich plot for adsorption of EB, EBT and CR on anion exchange membranes BII

Van't Hoff (Eq. (10)) equation (Yingjue *et al*. 2016, Vimonses *et al*. 2009)

$$\ln K_C = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{10}$$

$$K_C = \frac{C_a}{C_e} \tag{11}$$

$$\Delta G = \Delta H^o - T\Delta S^o \tag{12}$$

where K_C is the distribution coefficient of adsorption, R is the universal gas constant (8.314 J/mol.K), and T is the absolute temperature (K). C_e is the equilibrium concentration in solution (mg/L) and C_a is the solid phase concentration at equilibrium (mg/L). The plots of $\ln K_c$ verses $1/T$ for these anionic dyes with different initial concentration is given in Fig. 10. The values of ΔH^o (KJ/mol) and ΔS^o (KJ/mol.K) were calculated from slope and intercept of plot lnkc verses $1/T$ and are given in Table 3. The Gibb's free energy (ΔG^o) values for EB and EBT adsorption onto anion exchange membrane were measured from Eq. (12) and are given Table 3. It is found that the values of Gibb's free energy are positive for adsorption of anionic dyes EB and EBT onto anion exchange membrane. The Gibb's free energy (ΔG^o) values increases for both EB and EBT with increasing temperature as shown in Table 3. This may be due to interaction between the dyes on solid surface with non equal competition attributed to the heterogeneity of adsorbent surface and the system gained energy from external source at high temperatures. The values of enthalpy (ΔH^o) are negative for both anionic dyes adsorption onto BII indicating the exothermic nature of adsorption process. Similarly, the values of entropy (ΔS^o) for both EB and EBT are also negative suggesting the decrease in randomness at adsorbent-solution interface during adsorption.

Table 3 Thermodynamic parameters for adsorption of EB, EBT and CR on anion exchange membrane BII

System	C_o (mg/L)	ΔH (KJ/mol)	ΔS (J/mol)	ΔG (KJ/mol)		
				303 K	313 K	323 K
EB	25	-16.82	-25.34	7.66	7.91	8.16
	50	-13.69	-18.38	5.55	5.73	5.92
EBT	25	-38.31	-113.50	33.78	34.91	37.18
	50	-37.62	-113.62	33.89	35.03	37.30
CR	25	850.94	45.76	-12.78	-13.24	-13.70
	50	1250.48	63.48	-17.66	-18.30	-18.93

On the other hand, the Gibb's free energy (ΔG^o) values for CR adsorption onto anion exchange membrane BII were also calculated from Eq. (12) and are given in Table 3. It is clear that values of Gibb's free enery (ΔG^o) decreases with increase in temperature indicating the decrease in feasibility of adsorption at higher temperature. Moreover, the negative values of Gibb's free energy (ΔG^o) show that the adsorption of CR onto anion exchange membrane is spontaneous in nature. The positive values of ΔH^o shows that the adsorption of CR onto anion exchange membrane is endothermic process. Similarly the positive values of ΔS^o indicates the increase in randomness at the adsorbent-adsorbate interface during the CR adsorption onto anion exchange membrane.

4. Conclusions

The potential of anion exchange membrane BII for the removal of Eosin-*B*, Eriochrome Black-*T* and Congo Red dyes from aqueous solution has been investigated using batch system. The maximum dye removal was achieved using optimum experimental conditions of operating parameters such as contact time, membrane dosage, temperature and ionic strength. The percentage removal of anionic dyes increases with the contact time and reached maximum after 48 hours whereas maximum of removal of dyes were obtained using 0.1 g membrane dosage for all the systems. The rise of temperature decreases the removal of EB and EBT from 99.47% to 90.23% and 85.80% to 50.84% repectively from aqueous solution indicating the exothermic nature of EB and EBT adsorption. The removal of CR increases from 90.64% to 99.85% with rising temperature from 298 K to 328 indicating the endothermic nature of adsorption. The ionic strength had adverse affect on the removal of anionic dyes EB and EBT from aqueous solution by BIIwhereas the removal of CR by BII is not influenced by ionic strength. The adsorption kinetic data reveals that adsorption process fitted well to pseudo-second order kinetic model with highest numerical values of regression coefficient (R^2). The adsorption of dyes on membranes follows liquid film mechanism. The thermodynamics parameters for adsorption of these anionic dyes onto anion exchange membrane were calculated employing Van,t Hoff equation and positive value of Gibb's free energy for EB and EBT suggest that adsorption process is non spontaneous, on the other hand, the negative valueof Gibb's free energy for CR indicates the spontaneous nature of adsorption process. Moreover, positive value of entropy change (ΔS^o) shows the higher affinity of CR toward anion exchange membrane BII and increased randomness at adsorbent-adsorbate interface during adsorption. These results showed that the anion exchange membrane BII have a

great potential to be used as adsorbent for the anionic dyes (Eosin-*B*, Eriochrome Black-*T* and Congo Red from aqueous media.

Acknowledgements

Reference

Aharoni, C. and Ungarish, M. (1977), "Kinetics of activated chemisorption. Part 2.-Theoretical models", *J. Chem. Soc., Faraday Tran*., **73**(1), 456-464.

Ai, L., Li, M. and Li, L. (2011), "Adsorption of methylene blue from aqueous solution with activated carbon/cobalt ferrite/alginate composite beads: kinetics, isotherms, and thermodynamics", *J. Chem. Eng. Data*, **56**(8), 3475-3483.

Alireza, N.E. and Mahshid, K., (2010), "Heterogeneous photodecolorization of Eriochrome Black T using Ni/P zeolite catalyst", *Desalinat.*, **262**, 79-85

Alkan, M. and Doğan, M. (2001), "Adsorption of Copper(II) onto perlite", *J. Coll. Interf. Sci.*, **243**(2), 280-291.

Allègre, C., Moulin, P., Maisseu, M. and Charbit, F. (2006), "Treatment and reuse of reactive dyeing effluents", *J. Membr. Sci*., **269**(1-2), 15-34.

Aravindhan, R., Fathima, N.N., Rao, J.R. and Nair, B.U. (2007), "Equilibrium and thermodynamic studies on the removal of basic black dye using calcium alginate beads", *Coll. Surf. A: Physicochem. Eng. A*, **299**(1-3), 232-238.

Benselka-Hadj Abdelkader, N., Bentouami, A., Derriche, Z., Bettahar, N. and de Ménorval, L.C. (2011), "Synthesis and characterization of Mg-Fe layer double hydroxides and its application on adsorption of Orange G from aqueous solution", *Chem. Eng. J.*, **169**(1-3), 231-238.

Bouhamed, F., Elouear, Z. and Bouzid, J. (2012), "Adsorptive removal of copper(II) from aqueous solutions on activated carbon prepared from Tunisian date stones: Equilibrium, kinetics and thermodynamics", *J. Taiwan Inst. Chem. Eng*., **43**(5), 741-749.

Buckley, C. (1992), "Membrane technology for the treatment of dyehouse effluents", *Water Sci. Technol*., **25**(10), 203-209.

Bulut, E., Özacar, M. and Şengil, İ.A. (2008), "Adsorption of malachite green onto bentonite: Equilibrium and kinetic studies and process design", *Micr. Meso. Mater*., **115**(3), 234-246.

Chang, Y., Lai, J.Y. and Lee, D.J. (2016), "Thermodynamic parameters for adsorption equilibrium of heavy metals and dyes from wastewaters: Research updated", *Bioresour. Technol*., **222**, 513-516

Cheung, C.W., Porter, J.F. and McKay, G. (2000), "Sorption kinetics for the removal of copper and zinc from effluents using bone char", *Sep. Purif. Technol*., **19**(1-2), 55-64.

Chowdhury, S., Mishra, R., Saha, P. and Kushwaha, P. (2011), "Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk", *Desalinat.*, **265**(1-3), 159-168.

Clark, T., Bruce, M. and Anderson, S. (1994), "Decolorisation of extraction stage bleach plant effluent by combined hypochlorite oxidation and anaerobic treatment", *Water Sci. Technol*., **29**(5-6), 421-432.

Cooper, P. (1993), "Removing colour from dyehouse waste waters-a critical review of technology available", *J. Soc. Dyers Color*., **109**(3), 97-100.

Cortés-Martínez, R., Martínez-Miranda, V., Solache-Ríos, M. and García-Sosa, I. (2004), "Evaluation of natural and surfactant-modified zeolites in the removal of cadmium from aqueous solutions", *Sep. Sci.*

Technol., **39**(11), 2711-2730.

Crini, G. (2006), "Non-conventional low-cost adsorbents for dye removal: A review", *Bioresour. Technol.*, **97**(9), 1061-1085.

Doğan, M. and Alkan, M. (2003), "Adsorption kinetics of methyl violet onto perlite", *Chemosphere*, **50**(4), 517-528.

Ganna, D., Bénédicte, P., Amine, G., Louis-Charles, D. M. and Jerzy, Z. (2016), "Removal of three anionic orange-type dyes and Cr(VI) oxyanion from aqueous solutions onto strongly basic anion-exchange resin. The effect of single-component and competitive adsorption", *Coll. Surf. A: Physicochem. Eng. Aspects*, **508**, 240-250.

Gong, R., Ding, Y., Li, M., Yang, C., Liu, H. and Sun, Y. (2005), "Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution", *Dyes Pigm.*, **64**(3), 187-192.

Gupta, V.K., Ali, I., Saini, V.K., Van Gerven, T., Van der Bruggen, B. and Vandecasteele, C. (2005), "Removal of dyes from wastewater using bottom ash", *Ind. Eng. Chem. Res.*, **44**(10), 3655-3664.

Gupta, V.K., Mittal, A., Gajbe, V. and Mittal, J. (2006), "Removal and recovery of the hazardous azo dye acid orange 7 through adsorption over waste materials: bottom ash and de-oiled soya", *Ind. Eng. Chem. Res.*, **45**(4), 1446-1453.

Gupta, V.K., Srivastava, S.K. and Mohan, D. (1997), "Equilibrium uptake, sorption dynamics, process optimization, and column operations for the removal and recovery of malachite green from wastewater using activated carbon and activated slag", *Ind. Eng. Chem. Res.*, **36**(6), 2207-2218.

Gupta, V.K., Suhas, Ali, I. and Saini, V.K. (2004), "Removal of rhodamine B, fast green, and methylene blue from wastewater using red mud, an aluminum industry waste", *Ind. Eng. Chem. Res.*, **43**(7), 1740-1747.

Hamdaoui, O. (2006), "Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick", *J. Hazard. Mater.*, **135**(1-3), 264-273.

Ho, Y.S. (2006), "Second-order kinetic model for the sorption of cadmium onto tree fern: A comparison of linear and non-linear methods", *Water Res.*, **40**(1), 119-125.

Ho, Y.S. and McKay, G. (1999), "The sorption of lead(II) ions on peat", *Water Res.*, **33**(2), 578-584.

Hu, J., Song, Z., Chen, L., Yang, H., Li, J. and Richards, R. (2010), "Adsorption Properties of MgO(111) Nanoplates for the Dye Pollutants from Wastewater", *J. Chem. Eng. Data*, **55**(9), 3742-3748.

Jiraratananon, R., Sungpet, A. and Luangsowan, P. (2000), "Performance evaluation of nanofiltration membranes for treatment of effluents containing reactive dye and salt", *Desalinat.*, **130**(2), 177-183.

Kadirvelu, K., Karthika, C., Vennilamani, N. and Pattabhi, S. (2005), "Activated carbon from industrial solid waste as an adsorbent for the removal of Rhodamine-B from aqueous solution: Kinetic and equilibrium studies", *Chemosphere*, **60**(8), 1009-1017.

Kapdan, I.K. and Kargi, F. (2002), "Simultaneous biodegradation and adsorption of textile dyestuff in an activated sludge unit", *Proc. Biochem.*, **37**(9), 973-981.

Karadag, D., Akgul, E., Tok, S., Erturk, F., Kaya, M.A. and Turan, M. (2007), "Basic and reactive dye removal using natural and modified zeolites", *J. Chem. Eng. Data*, **52**(6), 2436-2441.

Karcher, S., Kornmüller, A. and Jekel, M. (2001), "Screening of commercial sorbents for the removal of reactive dyes", *Dyes Pigm.*, **51**(2-3), 111-125.

Karcher, S., Kornmüller, A. and Jekel, M. (2002), "Anion exchange resins for removal of reactive dyes from textile wastewaters", *Water Res.*, **36**(19), 4717-4724.

Khan, M.I., Akhtar, S., Zafar, S., Shaheen, A., Khan, M.I., Luque, R. and Rehama, A.U. (2015a), "Removal of Congo Red from Aqueous Solution by Anion Exchange Membrane (EBTAC): Adsorption Kinetics and Themodynamics", *Mater.*, **8**, 4147-4161.

Khan, M.I., Mondal, A.N., Chen, C., Pan, J., Emmanuel, K., Wu, L. and Xu, T. (2016c), "Porous BPPO-based membranes modified by aromatic amine for acid recovery", *Sep. Purif. Technol.*, **157**, 27-34.

Khan, M.I., Mondal, A.N., Emmanuel, K., Hossain, M.M., Afsar, N.U., Wu, L. and Xu, T. (2016b), "Preparation of pyrrolidinium-based anionexchange membranes for acid recovery via diffusion dialysis", *Sep. Sci. Technol.*, **51**, 1881-1890.

Khan, M.I., Mondal, A.N., Tong, B., Jiang, C., Emmanuel, K., Yang, Z., Wu, L. and Xu, T. (2016d), "Development of BPPO-based anion exchange membranes for electrodialysis desalination applications",

Desal., **391**, 61-68.

Khan, M.I., Wu, L., Hossain, M.M., Pan, J., Ran, J., Mondal. A.N. and Xu, T. (2015b), "Preparation of diffusion dialysis membrane for acid recovery via a phase-inversion method", *Membr. Water Treat.*, **6**, 365-378.

Khan, M.I., Wu, L., Mondal, A.N., Yao, Z., Ge, L. and Xu, T. (2016a), "Adsorption of methyl orange from aqueous solution on anion exchange membranes: Adsorption kinetics and equilibrium", *Membr. Wat. Treat.*, **7**, 23-38.

Khan, M.I., Zheng, C., Mondal, A.N., Hossain, M.M., Wu, B., Emmanuel, K., Wu, L. and Xu, T. (2017), "Preparation of anion exchange membranes from BPPO and dimethylethanolamine for electrodialysis", *Desal.*, **402**, 10-18.

Kheira, C., Kahina, B., Zohra, B., Abdelouahab, N. and Ulrich, M.,(2016), "Adsorption of reactive dyes from aqueous solution by dirty bentonite", *Appl. Clay Sci.*, **123**, 64-75.

Koyuncu, I. (2002), "Reactive dye removal in dye/salt mixtures by nanofiltration membranes containing vinylsulphone dyes: effects of feed concentration and cross flow velocity", *Desalinat.*, **143**(3), 243-253.

Kuo, S. and Lotse, E. (1973), "Kinetics of phosphate adsorption and desorption by hematite and gibbsite 1", *Soil Sci.*, **116**(6), 400-406.

Lin, J.X., Zhan, S.L., Fang, M.H., Qian, X.Q. and Yang, H. (2008), "Adsorption of basic dye from aqueous solution onto fly ash", *J. Environ. Manage.*, **87**(1), 193-200.

Liu, C.H., Wu, J.S., Chiu, H.C., Suen, S.Y. and Chu, K.H. (2007), "Removal of anionic reactive dyes from water using anion exchange membranes as adsorbers", *Water Res.*, **41**(7), 1491-1500.

Liu, H. L. and Chiou, Y.R. (2006), "Optimal decolorization efficiency of reactive red 239 by UV/ZnO photocatalytic process", *J. Chin. Inst. Chem. Eng.*, **37**(3), 289-298.

Lorenc-Grabowska, E. and Gryglewicz, G. (2007), "Adsorption characteristics of congo red on coal-based mesoporous activated carbon", *Dyes Pigm.*, **74**(1), 34-40.

Mall, I.D., Srivastava, V.C., Agarwal, N.K. and Mishra, I.M. (2005), "Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses", *Coll. Surf. A: Physicochem. Eng. A.*, **264**(1-3), 17-28.

Namasivayam, C. and Sumithra, S. (2005), "Removal of direct red 12B and methylene blue from water by adsorption onto Fe (III)/Cr (III) hydroxide, an industrial solid waste", *J. Environ. Manage.*, **74**(3), 207-215.

Namasivayam, C., Jeyakumar, R. and Yamuna, R.T. (1994), "Dye removal from wastewater by adsorption on 'waste' Fe(III)/Cr(III) hydroxide", *Waste Manage.*, **14**(7), 643-648.

Netpradit, S., Thiravetyan, P. and Towprayoon, S. (2003), "Application of 'waste' metal hydroxide sludge for adsorption of azo reactive dyes", *Water Res.*, **37**(4), 763-772.

Pala, A. and Tokat, E. (2002), "Color removal from cotton textile industry wastewater in an activated sludge system with various additives", *Water Res.*, **36**(11), 2920-2925.

Pelekani, C. and Snoeyink, V.L. (1999), "Competitive adsorption in natural water: role of activated carbon pore size", *Water Res.*, **33**(5), 1209-1219.

Plazinski, W., Rudzinski, W. and Plazinska, A. (2009), "Theoretical models of sorption kinetics including a surface reaction mechanism: A review", *Adv. Coll. Interf. Sci.*, **152**(1-2), 2-13.

Robinson, T., McMullan, G., Marchant, R. and Nigam, P. (2001), "Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative", *Bioresour. Technol.*, **77**(3), 247-255.

Silvia, P.D.M., Blanco, F.B.S., Aparecido, N.M., Fernando, R.E.Q., Pricila, M.A.D.K. and Carlos, E.B. (2017), "Kinetic, equilibrium and thermodynamic phenomenological modeling of reactive dye adsorption onto polymeric adsorbent", *Chem. Eng. J.*, **307**, 466-475

Solozhenko, E.G., Soboleva, N.M. and Goncharuk, V.V. (1995), "Decolourization of azodye solutions by Fenton's oxidation", *Water Res.*, **29**(9), 2206-2210.

Treffry-Goatley, K., Buckley, C.A. and Groves, G.R. (1983), "Reverse osmosis treatment and reuse of textile dyehouse effluents", *Desalinat.*, **47**(1-3), 313-320.

Tütem, E., Apak, R. and Ü nal, Ç .F. (1998), "Adsorptive removal of chlorophenols from water by bituminous

shale", *Water Res.*, **32**(8), 2315-2324.

Vimonses, V., Lei, S., Jin, B., Chow, C.W.K. and Saint, C. (2009), "Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials", *Chem. Eng. J.,* **148**(2-3), 354-364.

Zhang, J., Zhou, Q. and Ou, L. (2012), "Kinetic, isotherm, and thermodynamic studies of the adsorption of methyl orange from aqueous solution by chitosan/alumina composite", *J. Chem. Eng. Data*, **57**(2), 412-419.

CC

Nomenclature

Code	Full name
EB	Eosin *B*
EBT	Erichrome Black *T*
CR	Congo Red
AEM	Anion exchange membrane
IEC	Ion exchange capacity
W_R	Water uptake
PVA	Polyvinyl alcohal
QPPO	Quaternized poly(2,6-dimethyl-1,4-phenylene oxide)
C_o	Initial dye concentration (mg/L)
C_e	Dye concentration in solution (mg/L) at time t
q_t	Adsorption capacity at time "t"
q_e	Adsorption capacity at equilibrium
R^2	Correlation coefficient
$(q_{e,\ exp})$	Experimental data of equilibrium capacity (mg/g)
$(q_{e,\ cal})$	Equilibrium capacity obtained by calculating the isothermal model (mg/g)
k_1	First order rate constant (/min)
k_2	Second order rate constant (g/mg/min)
α	Chemi-sorption rate (/mg.min)
β	Desorption constant (g/min)
K_{fd}	Liquid film diffusion rate constant
t	Time in minutes
V	Liquid phase volume (L)
W	weight of adsorbent (g)
K_C	Distribution coefficient of adsorption
T	Absolute temperature (K)
R	Universal gas constant
ΔG^o	Free energy change of adsorption reaction (KJ/mol)
ΔH^o	Enthalpy change of adsorption reaction (KJ/mol)
ΔS^o	Entropy change of adsorption reaction (J/mol K)