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Adsorptive removal of anionic dyes in aqueous binary mixture by anion exchange membrane

Hina Masood[a], Shagufta Zafar[a,*], Hafeez ur Rehman[b], Muhammad Imran Khan[c,*], Hafiz Badaruddin Ahmad[d], Aqsa Naz[a], Warda Hassan[e], Mushtaq Hussain Lashari[f,*]

[a]*Department of Chemistry, The Government Sadiq College Women University, Bahawalpur 63000, Pakistan, emails: shg_zf@gscwu.edu.pk (S. Zafar), hinamasood234@gmail.com (H. Masood), nazaqsa194@gmail.com (A. Naz)*
[b]*Department of Economics, The Islamia University of Bahawalpur, Bahawalpur 63100, Pakistan, email: hafeez.rehman@iub.edu.pk (H. ur Rehman)*
[c]*School of Energy and Power Engineering, Xi'an Jiaotong University, 28 West Xianning Road, Xi'an 710049, Shaanxi, PR. China, email: raoimranishaq@gmail.com (M.I. Khan)*
[d]*Institute of Chemical Sciences, Bahauddin Zakariya University, Multan, Pakistan, email: hafizbadar@gmail.com (H.B. Ahmad)*
[e]*Department of Chemistry, The Women University of Multan, Multan, Pakistan, email: wardahassan42@yahoo.com (W. Hassan)*
[f]*Department of Zoology, The Islamia University of Bahawalpur, Bahawalpur 63100, Pakistan, email: mushtaqlashary@gmail.com (M.H. Lashari)*

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ABSTRACT

In the present research, batch adsorption of anionic dyes such as Congo red (CR) and Acid Black 210 (AB210) in aqueous binary mixture onto anion exchange membrane (AEM) BIII was investigated at room temperature. The effect of various physico-chemical parameters such as contact time, membrane dosage, initial dye concentration, and temperature on the percentage removal of dyes was investigated. Adsorption kinetics was revealed using linear and nonlinear form of pseudo-first-order and pseudo-second-order models but experimental data for adsorption of CR and AB 210 in aqueous binary mixture onto AEM BIII fitted well to pseudo-first-order model. Linear and nonlinear forms of Langmuir, Freundlich, Tempkin, and Dubinin–Radushkevich (D–R) were used to reveal experimental data but experimental data for adsorption of CR and AB 210 in aqueous binary mixture onto AEM BIII fitted well to the Langmuir isotherm model. Adsorption thermodynamic study showed that adsorption of CR and AB210 onto AEM BIII was an endothermic and spontaneous process. Desorption of CR and AB210 was also studied at ambient temperature.

Keywords: Binary system; Anion exchange membrane; Adsorption; Thermodynamics; Isotherms

1. Introduction

Today's world demands sustainable water supply because of the lesser presence of freshwater and pollutant discharged into the environment from different factories. Any unwanted addition of chemical substances into water bodies leads to its pollution and becomes unsuited for human applications [1]. Among the different pollutants released to the environment, dyes can be regarded as one of the most dangerous contaminants. The dyes are more stable, highly toxic, and carcinogenic and their discharge into the environment poses adverse effects, even at low concentrations [2,3]. Dyes are usually divided into three main categories: anionic (direct, acid, and reactive dyes), cationic (all basic dyes), and non-ionic (dispersed dyes).

* Corresponding authors.

Reactive dyes are largely employed for dyeing of fibres as it is very economical and less toxic, but its drainage causes severe environmental issues [4–6].

Several techniques such as flocculation and coagulation [7], ozonation or oxidation [8], photocatalytic degradation [9], micellar enhanced ultrafiltration [10], membrane separation [11], electrochemical degradation [12], sonochemical degradation [13], Fenton-biological treatment scheme [14], solar photo-Fenton and biological processes [15] and adsorption have been employed for removal of dyes [1,16]. Adsorption has gained tremendous popularity over conventional techniques because of less capital investment, ease of operation, the flexibility of design, and insensitivity to toxic pollutants from the reported methods [17]. Previous research has shown the utilization of many adsorbents such as ion-exchange resins, plant leaf, clay, activated carbon, and zeolites [18–23]. From one adsorbent to others, their price and efficiency changed.

Among the present technologies, ion-exchange membranes (IEMs) based separation methods are the most crucial. Ion exchange membranes can be divided into anion exchange membrane (AEM) and cation exchange membrane (CEM). Presently, commercial AEMs have been defined to have distinguished adsorption capacities. All the adsorbents prepared for the discharge of heavy metal ions and dyes based on the interaction of the target compounds with the functional groups that are located on the surfaces of the adsorbents [24]. Hence, a large surface area and many adsorption sites of the matrix are essential for the adsorption affinity of membranes to discharge the contaminants from wastewater, and the special surface area was one of the most important endowments to affect the adsorption capacity of the adsorbents [25–27]. Therefore, the AEM becomes an excellent choice as an adsorbent for dye discharge from aqueous solution due to it represents large surface area for adsorption. Two types of membranes such as P81 and ICE450 were employed for the discharge of cationic dye methyl violet 2B from aqueous solution via the adsorption process [28]. Similarly, the AEM was prepared for the adsorptive discharge of anionic dye Cibacron Blue 3GA from aqueous solution [29].

Our previous work reported the use of several plant leaves and AEMs for the removal of dyes from aqueous solution at room temperature [30–33]. This research describes the use of AEM BIII as an excellent adsorbent for removal of CR and AB210 in the aqueous binary mixture at ambient temperature. The effect of operating endowments onto the percentage removal of anionic dyes was revealed. Attained experimental data was subjected to linear and nonlinear forms of kinetic models. Adsorption equilibrium was revealed using linear and nonlinear forms of Langmuir, Freundlich, Tempkin, and Dubinin–Redushkevich (D–R) isotherms. Moreover, the experimental data were also subjected to thermodynamics analysis. Desorption of dyes (CR and AB210) was also analyzed.

2. Experimental

2.1. Adsorbent

Herein, the commercial AEM BIII was used as adsorbent for the removal of CR and AB210 from aqueous binary solution. It was supplied by Chemjoy Membrane Co., Ltd., Hefei, Anhui, China. The ion exchange capacity and water uptake of AEM BIII are 0.26 mmol/g and 33%, respectively. Its polymer backbone is blends of quaternized poly (2,6-dimethyl-1,4-phenylene oxide) and polyvinyl alcohol with weight ratio of and 3:7 and was reinforced by woven polyester fibers [34].

2.2. Adsorbate

In this work, anionic dyes including Congo red and Acid Black 210 were employed as adsorbate. Both CR and AB210 were supplied by Fluka chemicals. The values of wavelengths (λ_{max}.) used for Congo red and AB210 are 510 and 610 nm respectively. Fig. 1 represents the molecular structure of CR and AB210.

2.3. Adsorption test

In this research, batch adsorption test was carried out as reported in our previous work [30,32,33,35]. It was performed by immersing AEM BIII into known volume and concentration of dyes solution at room temperature. The culture tubes were shaken at a constant speed of 120 rpm and concentration of binary mixture of dyes was measured using UV/VIS spectrophotometer and related calibration curves were obtained at the wavelength 510 nm for CR and 610 nm for AB210. The amount of dyes adsorbed in binary mixture onto AEM BIII at time *t*, was calculated by below relationship:

$$Q_t = \frac{\left(C_0 - C_t\right) \times V}{W} \tag{1}$$

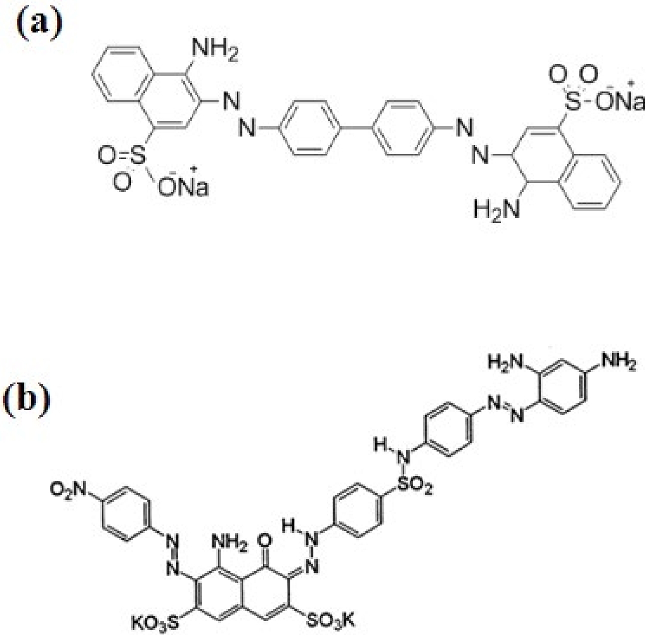


Fig. 1. Molecular structure of (a) CR and (b) AB210 dye.

The percentage adsorption can be measured by the following expression:

$$w\%\ \text{adsorption} = \frac{\left(C_0 - C_e\right)\times 100}{C_0} \quad (2)$$

where C_0 and C_e are initial and equilibrium concentration of dye respectively and C_t is the concentration of dyes at time t. Similarly, V and W are volume dyes and weight of AEM, respectively.

3. Results and discussion

3.1. Effect operating parameters

The influence of operating endowments on the percentage removal of CR and AB210 in aqueous binary mixture is given below.

3.1.1. Effect of contact time

The effect of contact time on the percentage removal of CR and AB210 in aqueous binary mixture by AEM BIII was investigated keeping membrane dosage (0.2 g), dye concentration (75 mg/L), volume of solution (30 mL) and stirring speed (120 rpm) constant at room temperature and attained results are shown in Fig. 2a. It has been observed that the removal of CR was 29%–72% whereas the removal of AB210 was18%–52%. For both dyes in a binary mixture, the removal was found to be increased with increasing contact time. It is due to the presence of several adsorption sites onto the membrane surface in the initial stage of reaction, which gradually gets saturated with the dye at increasing contact times. The percentage removal of CR in the aqueous binary mixture was higher than AB210 because of their different properties and chemical structures. The anionic dye CR have two sulfonic groups that can be attached with two ion-exchange groups thus making strong bond with the adsorbent (AEM BIII). Moreover, amino groups present in the CR are electron-donating which facilitates the interaction of sulfonic groups with ion exchange membrane resulting in higher removal of CR in an aqueous binary mixture. On the other hand, the nitro group (NO_2) attached with it is an electron withdrawing thus deactivating the interaction between AB210 and ion exchange membrane leading to lower adsorption of AB210.

3.1.2. Effect of membrane dosage

Fig. 2b depicts the percentage removal of CR and AB210 in the aqueous binary mixture as a function of membrane dosage at ambient temperature. It was investigated keeping other operating parameters constant. From the attained results, it can be seen that the percentage removal of CR was enhanced from 21% to 75% whereas the percentage removal of AB210 was increased from 31% to 74% with increasing the membrane dosage from 0.02 to 0.3 g. The enhancement in the adsorption of dyes was due to the increase in the number of available adsorption sites onto the surface of the AEM [32].

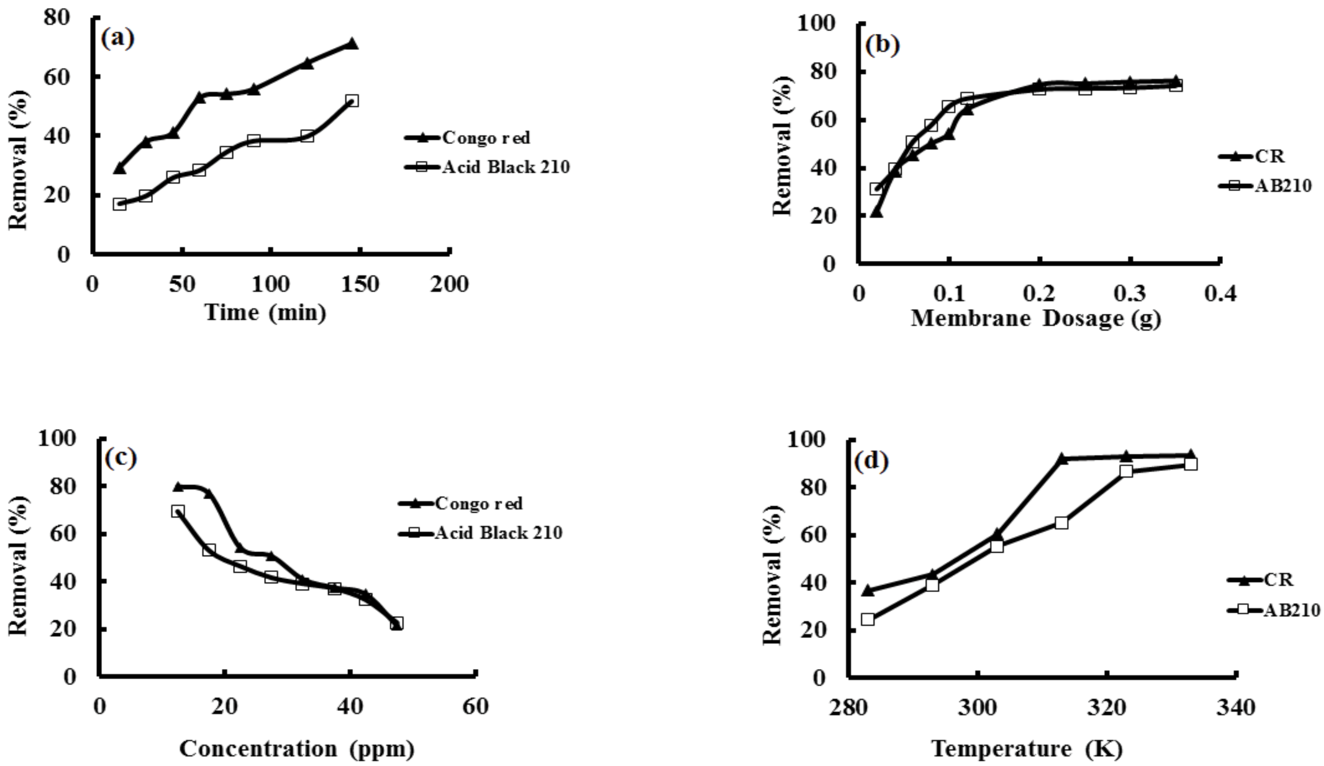


Fig. 2. Effect of (a) contact time, (b) membrane dosage, (c) initial dye concentration, and (d) temperature onto the removal of CR and AB210 anion exchange membrane BIII.

Initially, the removal of CR and AB210 dye was fast, reaching equilibrium remaining almost unchanged with a further increase in the membrane dosage. At 0.2 g of membrane dosage, the maximum removal of CR and AB210 was achieved. Beyond this amount of membranes, there was no significant change. Hence, 0.2 g was selected as an optimum mass of AEMs. This optimum mass of BIII was employed in further study.

3.1.3. Effect of initial concentration

The effect of the initial concentration of dyes in the binary mixture on the percentage removal was investigated keeping membrane dosage, contact time, the volume of solution, and stirring speed constant at room temperature, and attained results are represented in Fig. 2c. It has been observed that the removal of CR and AB210 in the aqueous binary mixture was decreased by increasing initial dye concentration from 25 to 95 mg/L. The removal of CR was decreased from 81% to 21% whereas the removal of AB210 was decreased from 70% to 22% in an aqueous binary mixture. It is attributed to an increase in the concentration of dyes in aqueous binary mixture, surface area, and active sites of BIII were saturated [32].

3.1.4. Effect of temperature

Fig. 2d represents the influence of temperature on the percentage removal of CR and AB210 in aqueous binary mixture by AEM BIII. The effect of temperature on the percentage removal of binary mixture of dyes from aqueous solution was studied keeping all other parameters constant. It can be observed from Fig. 2d that the removal of CR and AB210 was found to be increased from with increasing the temperature from 293 to 333 K. The removal of CR was increased from 36% to 93% whereas the removal of AB210 was increased from 25% to 90% with increasing temperature. It shows that high temperature favors the removal of CR and AB210 from aqueous solution. It is due to the decrease in solubility of dyes with increasing temperature. Moreover, the increase in temperature increases the mobility of large dye ions which may be responsible to increase adsorption of dyes. An increasing number of molecules may acquire sufficient energy to undergo an interaction with active sites at the surface. It depicts that adsorption of CR and AB210 onto AEM BIII is an endothermic process.

3.2. Adsorption kinetics

The kinetic study is important for the adsorption process, it describes the uptake rate of adsorbate on the adsorbent and controls the time of the whole adsorption process. The kinetic parameters are helpful for the prediction of adsorption rate, which gives important information for designing and modeling the processes.

3.2.1. Pseudo-first-order model

The linearized form of pseudo-first-order kinetic model is generally expressed as [36]:

$$\log\left(q_e - q_t\right) = \log q_e - k_1 t \tag{3}$$

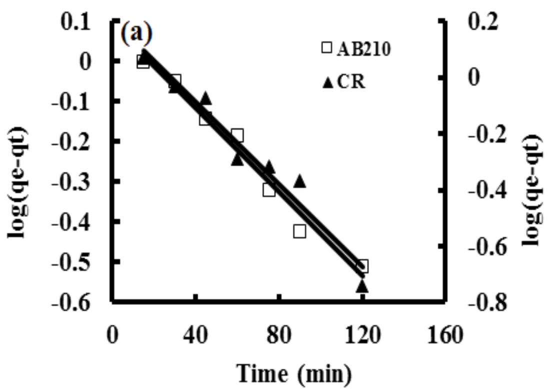
The nonlinear form of pseudo-first-order kinetic model is shown as:

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{4}$$

where q_e and q_t depicts the amounts of dye adsorbed at equilibrium and time t respectively, k_1 (1/min) is the rate constant of pseudo-first-order adsorption model. The plot of log(q_e – q_t) vs. time for adsorption of CR and AB210 in aqueous binary system onto AEM BIII is shown in Fig. 3a. The values of k_1 for adsorption of CR and AB210 in aqueous binary system onto AEM BIII were measured from slope of Fig. 3a and are given in Table 1. For pseudo-first-order model, the values of correlation coefficient (R^2) were 0.978 and 0.956 for AB1 and CR, respectively. Contrary, the parameters for nonlinear form of pseudo-first-order equation was determined by wave matrix software IGOR PRO 6.1.2 and given in Table 2 and plot for it is represented in Fig. 4a.

3.2.2. Pseudo-second-order model

The linearized form of pseudo-second-order kinetic model is represented as [37,38]:



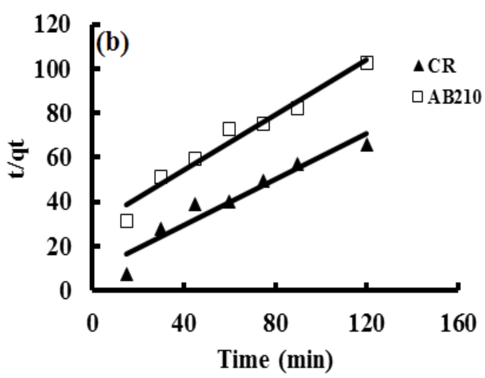


Fig. 3. Linear plot of (a) pseudo-first-order kinetic model and (b) pseudo-second-order kinetic model for adsorption of CR and AB210 in aqueous binary system onto anion exchange membrane BIII.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

The nonlinear form of pseudo-second-order kinetic model is depicted as:

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \tag{6}$$

where k_2 (g/mg min) is the rate constant of pseudo-second-order kinetic model, q_e is the adsorption capacity, q_t is the amount of dye adsorbed at equilibrium. Fig. 3b depicts the plot of time vs. t/q_t for adsorption of CR and AB210 in aqueous binary system onto AEM BIII. For both dyes in binary system, the values of adsorption capacity (q_e) was determined from slope whereas the values of rate constant (k_2) were calculated from intercept of t/q_t vs. time and are given in Table 1. The values of correlation coefficient were 0.961 and 0.923 for AB210 and CR, respectively. These values are lower than pseudo-first-order model which showed that experimental data was not fitted well to the pseudo-second-order model. On the hand, the parameters for nonlinear form of pseudo-second-order equation were determined by wave matrix software IGOR PRO 6.1.2 and are given in Table 2 and plot for it is shown in Fig. 4b.

Table 1
Pseudo-first-order and pseudo-second-order kinetic parameters for adsorption of CR and AB210 on anion exchange membrane BIII by linear method. (q_e: mg/g; k_1: /min; k_2: g mg/min)

Kinetic models		Congo Red		Acid Black 210
Pseudo-first-order model	q_e	1.604	q_e	1.24
	k_1	0.016121	k_1	0.0115
	R^2	0.956	R^2	0.978
Pseudo-second-order model	q_e	1.95	q_e	1.6
	k_2	0.0293	k_2	0.014
	R^2	0.923	R^2	0.961

3.3. Adsorption isotherms

The proper quantification of adsorption procedure is required for application of adsorption process on the commercial level. Adsorption equilibrium is necessary for the analysis and design of the adsorption process. It provides fundamental data of physicochemical method for evaluating the applicability of the process as a unit operation. Herein, Langmuir, Freundlich, Tempkin, and Dubinin–Radushkevich adsorption isotherms were employed to reveal experimental data.

3.3.1. Langmuir adsorption isotherm

The Langmuir isotherm has been used by various workers for adsorption study of a variety of systems [39]. Langmuir model supposes homogeneity of adsorbing surface and no interactions between adsorbed species having uniform

Table 2
Pseudo-first-order and pseudo-second-order kinetic parameters for adsorption of CR and AB210 in aqueous binary mixture on anion exchange membrane BIII by nonlinear method. (q_e: mg/g; k_1: /min; k_2: g mg/min)

Kinetic models		Congo Red		Acid Black 210
Pseudo-first-order model	q_e	1.95 ± 6.13	q_e	1.6807 ± 0.26
	k_1	0.02 ± 0	k_1	0.013102 ± 0.00362
	χ^2	0.147167	χ^2	0.0476444
Pseudo-second-order model	q_e	2.1167 ± 0.131	q_e	2.3383 ± 0.429
	k_2	0.017652 ± 0.00459	k_2	0.0045739 ± 0.00236
	χ^2	0.0193298	χ^2	0.0380868

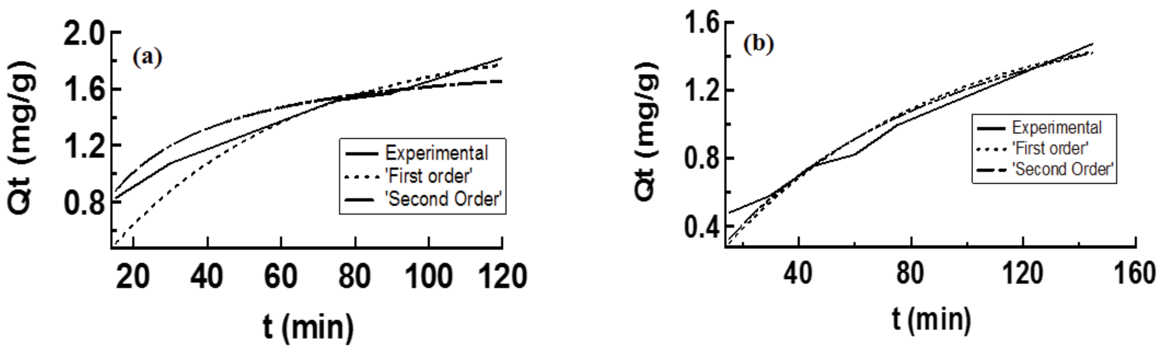


Fig. 4. Nonlinear plot of pseudo-first-order and pseudo-second-order kinetic model for adsorption of (a) CR and (b) AB210 in aqueous binary mixture onto anion exchange membrane BIII.

energies of adsorption onto the surface and no transmigration of adsorbate species in the plane of the surface. The difference in adsorption capacities of two adsorbents for same sorbate is believed to be largely due to the physicochemical properties of them or the chemistry of solution containing adsorbing species.

The nonlinear form of Langmuir adsorption isotherm may be expressed as:

$$C_{\text{ads}} = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

The Eq. (7) non-linear Langmuir isotherm can be linearized as:

$$\frac{C_e}{C_{\text{ads}}} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (8)$$

where C_e is the concentration of dyes solution (mol/L) at equilibrium and C_{ads} is the amount adsorbed per unit mass onto adsorbent at equilibrium (mol/g). The constant Q_m is monolayer adsorption capacity (mol/g) and K_L (L/mol) is related to the energy of adsorption. In general, Q_m and K_L are functions of pH, ionic media, and ionic strength. The values of Q_m for adsorption of CR and AB210 in aqueous binary mixture onto AEM BIII were computed by nonlinear and linear forms of Langmuir isotherm. Wavemetrices IGOR Pro 6.1.2 software was used for the calculation of isotherm parameters while using nonlinear equations. The nonlinear form of Langmuir isotherm model for adsorption of CR and AB210 in aqueous binary mixture onto AEM BIII is represented in Fig. 5 and the attained constants are given in Table 3. Similarly, the linearized form of Langmuir isotherm model for adsorption of CR and AB210 in aqueous binary mixture onto BIII is represented in Fig. 6a and attained endowments is given in Table 4. To compare the application of different forms of the models, the regression coefficient "R^2" and Chi-square test "χ^2" were used as determining tools for the best-fit of adsorption isotherm equations which may be measured by the below relationships:

$$R^2 = \frac{\Sigma(C_{\text{ads,cal}} - \acute{C}_{\text{ads,exp}})^2}{\Sigma(C_{\text{ads,cal}} - \acute{C}_{\text{ads,exp}})^2 - \Sigma(C_{\text{ads,cal}} - C_{\text{ads,exp}})^2} \quad (9)$$

$$\chi^2 = \Sigma \frac{\left(C_{\text{ads}} - C_{\text{ads,m}}\right)^2}{C_{\text{ads,m}}} \quad (10)$$

where $C_{\text{ads,exp}}$ is experimental adsorption at time t (mol/g), $C_{\text{ads,cal}}$ is calculated adsorption at time t (mol/g), $\acute{C}_{\text{ads,exp}}$ is average of $C_{\text{ads,exp}}$. (mol/g), C_{ads} is equilibrium capacity from experimental data (mol/g), and $C_{\text{ads},m}$ is calculated equilibrium capacity from the model (mol/g). The computed value of "R^2" for linear equation is given in Table 4 and Chi-square "χ^2" for nonlinear equation is shown in Table 3. The similarity of the data obtained from a nonlinear model is usually established by comparison with the experimental data, χ^2 would be a smaller number and vice versa, whereas for linear models, maximum value of "R^2" is considered to be more favorable.

An important endowment of a Langmuir isotherm can be expressed in terms of a dimensionless constant "separation factor" parameter, "R_L" that is used to predict if an adsorption system is "favorable" or "unfavorable" and can be expressed as follows:

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

where C_0 is the initial concentration of metal ions (mol/L) and K_L is the Langmuir adsorption equilibrium constant (L/mol). The value of R_L indicates adsorption process to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The values of R_L for adsorption of CR and AB210 in aqueous binary mixture onto AEM BIII was calculated from Langmuir constant K_L and initial concentrations of metal ion and results are summarized in Table 4 which confirms that adsorption of CR and AB210 in aqueous binary mixture onto BIII was favorable indicated by the fractional values of R_L between one and zero.

3.3.2. Freundlich isotherm model

Freundlich isotherm was proposed by Herbert F. Freundlich which is mathematically defined as:

$$C_{\text{ads}} = K_f C_e^{1/n} \quad (12)$$

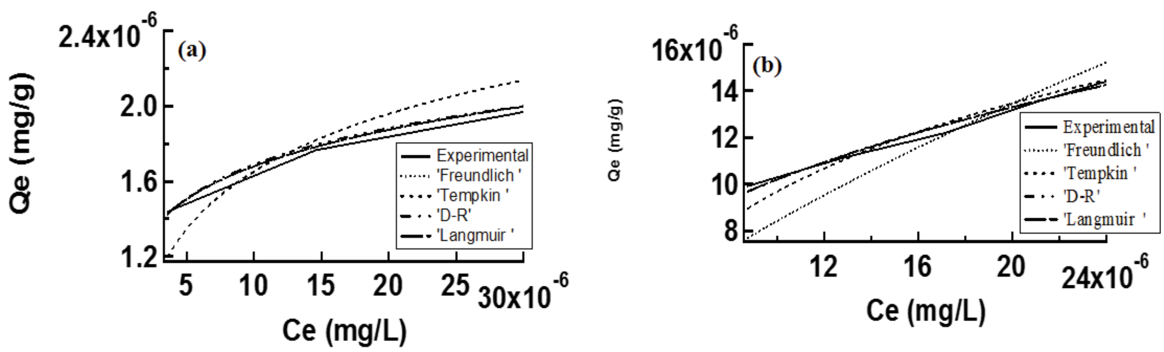


Fig. 5. Nonlinear plots of Langmuir, Freundlich, Tempkin, and D–R isotherms for adsorption of (a) CR and (b) AB210 in aqueous binary mixture onto anion exchange membrane BIII.

Table 3
Langmuir, Freundlich, Tempkin, and D–R isotherms parameters for adsorption of CR and AB210 in aqueous binary mixture on anion exchange membrane BIII by nonlinear method. (Q_m: mg/g; K_L: L/mol; K_F: mol/g; b_T: KJ/mol; A_T: L/mg; β: mol²/J²; C_m: mg/g; E: KJ/mol)

Isotherms	Congo Red		Acid Black 210	
Langmuir isotherm	Q_m	$0.77376 \pm 1.52 \times 10^{-5}$	Q_m	2.6101 ± 0.196
	K_L	$0.080252 \pm 1.58 \times 10^{+5}$	K_L	0.00083951 ± 0.000264
Freundlich isotherm	n	6.3299 ± 0.338	n	$1.4759 \pm 2.16 \times 10^{-10}$
	K_F	$1.0354 \times 10^{-5} \pm 9.45 \times 10^{-7}$	K_F	$0.020542 \pm 2.1 \times 10^{-9}$
	χ^2	1.359×10^{-15}	χ^2	1.123×10^{-13}
Tempkin isotherm	A_T	$4.1644 \times 10^{+5} \pm 1.1 \times 10^{+5}$	A_T	$3.6179 \times 10^{+5} \pm 1.41 \times 10^{+6}$
	b_T	$5.5382 \times 10^{+6} \pm 1.61 \times 10^{+5}$	b_T	$5.5475 \times 10^{+6} \pm 1.34 \times 10^{+5}$
	χ^2	1.141×10^{-13}	χ^2	2.7842×10^{-13}
D–R isotherm	C_m	$4.264 \times 10^{-7} \pm 2.5 \times 10^{-7}$	C_m	$0.00010072 \pm 1.73 \times 10^{-5}$
	β	$0.0011603 \pm 8.24 \times 10^{-5}$	β	0.0028743 ± 0.000237
	χ^2	2.374×10^{-15}	χ^2	2.7842×10^{-13}
	E	9.8	E	13.6

Table 4
Langmuir, Freundlich, Tempkin, and D–R isotherms parameters for adsorption of CR and AB210 in aqueous binary mixture on anion exchange membrane BIII by linear method. (Q_m: mg/g; K_L: L/mol; K_F: mol/g; b_T: KJ/mol; A_T: L/mg; β: mol²/J²; C_m: mg/g; E: KJ/mol)

	Congo Red		Acid Black 210	
Langmuir Isotherm	Q_m	2.414×10^{-5}	Q_m	1.717×10^{-5}
	K_L	5.5144×10^{-4}	K_L	1.798×10^{-6}
	R^2	0.993	R^2	0.978
	R_L	0.014–0.035	R_L	0.042–0.068
Freundlich Isotherm	n	2.95	n	6.494
	K_F	14.22	K_F	16.854
	R^2	0.941	R^2	0.971
Tempkin Isotherm	b_T	4.567	b_T	7.432
	A_T	125.672	A_T	54.26
	R^2	0.930	R^2	0.963
D–R Isotherm	Q_{DR}	0.00265	Q_{DR}	0.00168
	β	0.005	B	0.001
	E	11.53	E	19.5
	R^2	0.935	R^2	0.959

The linearized form of Freundlich isotherm:

$$\log C_{\text{ads}} = \log K_f + \frac{1}{n} \log C_e \tag{13}$$

where C_e is concentration of adsorbate at equilibrium in aqueous solution (mol/) and C_{ads} is adsorbed concentration per unit mass of adsorbent (mol/g). "K_F" and "n" are Freundlich constants indicating adsorption capacity and adsorption intensity, respectively. The good fit of adsorption data to Freundlich isotherm indicates that there is almost no limit to the amount adsorbed and multilayer adsorption will occur. The nonlinear form of Freundlich isotherm is for adsorption of CR and AB210 onto the AEM depicted in Fig. 5 and attained values of K_F and n are given in Table 3. On the other hand, the linear form of Freundlich adsorption isotherm for the adsorption of CR and AB210 in aqueous binary mixture onto BIII is represented in Fig. 6b and attained parameters are given in Table 4. The value of n signifies the heterogeneous surface of the anion exchange membrane BIII. The values of "n" ranges from 2 to 10 indicating good adsorption, 1 to 2 moderate adsorption, and less than one indicates poor adsorption [40].

3.3.3. Tempkin isotherm model

The Tempkin isotherm assumes that the heat of adsorption of all the molecules decreases linearly with the coverage of the molecules due to the adsorbate–adsorbate repulsion and the adsorption of adsorbate is uniformly distributed and that the fall in the heat of adsorption is linear rather than logarithmic [41]. The nonlinear form of Tempkin isotherm is represented as:

$$Q_t = \frac{RT}{b_T} \ln A_T C_e \tag{14}$$

The linearized form of isotherm is shown as:

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \tag{15}$$

where q_e is amount adsorbed per gram, R is general gas constant, T is absolute temperature. The constant b_T is related to the heat of adsorption and A_T is equilibrium binding constant coinciding to the maximum binding energy. The nonlinear plot of Tempkin isotherm for adsorption of CR and AB210 onto AEM BIII is represented in Fig. 5 and attained values of A_T and b_T are given in Table 3. Moreover, the lower values of Chi-square depicted that adsorption of CR and AB210 onto AEM BIII obeyed Tempkin isotherm. Contrary, Fig. 6c represents the plot for adsorption of CR and AB210 onto AEM BIII by the linear method. The values of

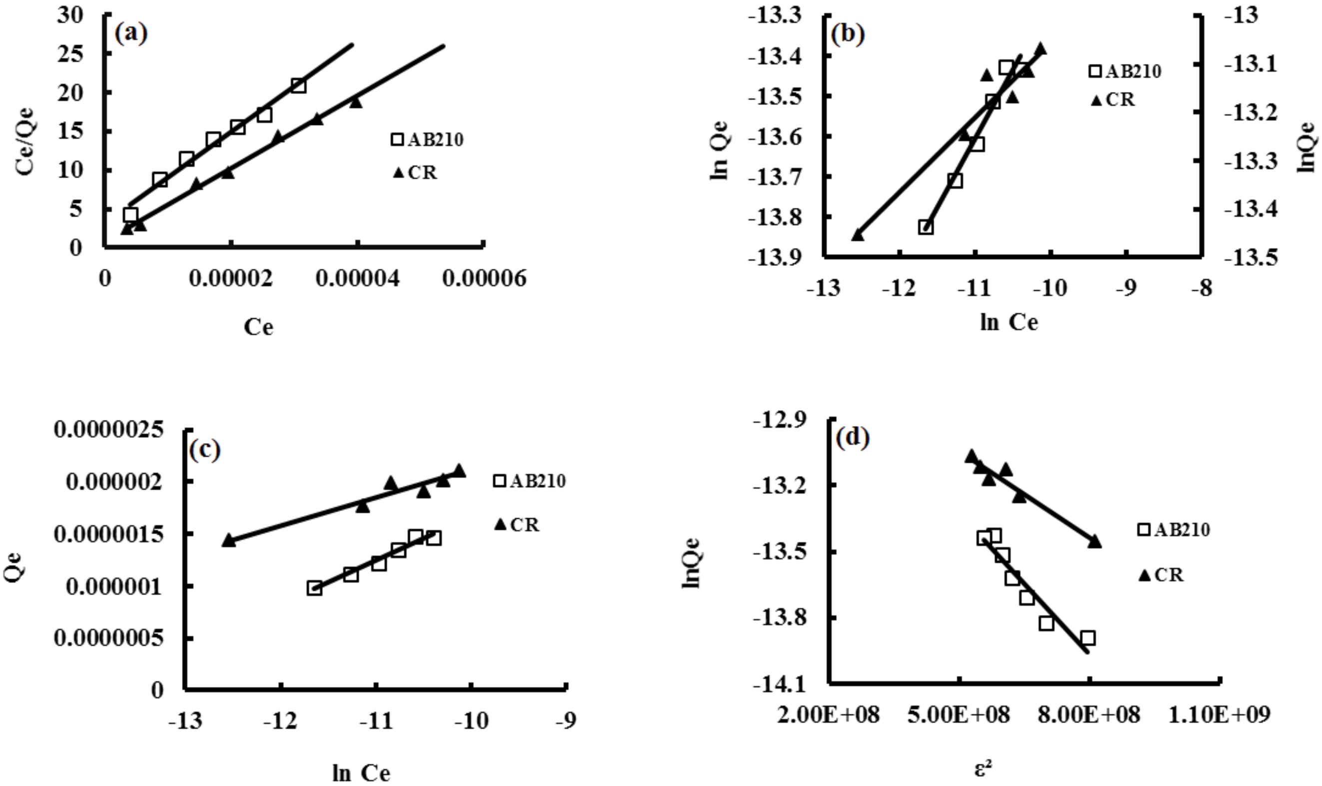


Fig. 6. (a) Langmuir isotherm, (b) Freundlich isotherm, (c) Tempkin isotherm, and (d) D–R isotherm for adsorption of CR and AB 210 in aqueous binary mixture onto anion exchange membrane BIII.

endowments b_T and A_T are given in Table 4. The higher values of the correlation coefficient exhibited that adsorption of CR and AB210 onto AEM BIII obeyed Tempkin isotherm.

3.3.4. Dubinin–Radushkevich model

The nonlinear D–R equation can be represented as:

$$C_{\text{ads}} = C_m \exp\left(-\beta\varepsilon^2\right) \quad (16)$$

where C_{ads} is the amount of dyes adsorbed onto AEM BIII, C_m (mol/g) is the maximum amount of dyes that can be adsorbed onto AEM BIII under the optimized experimental conditions, β is a constant related to sorption energy and ε (Polyanyi potential) = $RT \ln\left(1+\frac{1}{C_e}\right)$ where R is the universal gas constant (kJ/mol K), T is the absolute temperature (K) and C_e is the equilibrium concentration of metal ions in solution (mol/g). The linearized form of D–R isotherm:

$$\ln C_{\text{ads}} = \ln C_m - \beta\varepsilon^2 \quad (17)$$

From β value, the mean adsorption energy (E) can be computed as [42]:

$$E = \frac{1}{\sqrt{2\beta}} \quad (18)$$

which is the mean free energy of transfer of one mole of solute from infinity to the surface of adsorbent.

Fig. 5 depicted the nonlinear plot for adsorption of CR and AB210 in aqueous binary mixture onto AEM BIII. Computer program Wavemetrices Igor Pro 6.2.1.2 was used to measure D–R constant for nonlinear form of the plot of C_{ads} vs. C_e and are given in Table 3 along with their respective (χ^2) values which can be used as best fitting tool in nonlinear method. The values of "C_m" and "β" along with calculated adsorption free energy are also given in Table 3. Low numerical values of "χ^2"for nonlinear and high values of "R^2" for linear plots represented that the experimental data obeyed well.

The plots of a straight line for adsorption of CR and AB210 in aqueous binary mixture onto AEM were obtained by using the linear form of D–R isotherm of Eq. (17) and are presented in 6 d. The values of C_m and β were calculated from intercepts and slopes of plot of lnC_{ads} vs. ε^2 using a least-square fit program and are given in Table 4. The D–R constants (C_m) for adsorption of CR and AB210 in aqueous binary mixture onto BIII were 0.00265 mol/g and 0.00168 mg/g, respectively evaluated from intercept of straight lines using least square fit program.

The β values were used for the determination of adsorption free energy (E) for adsorption of CR and AB210 onto AEM BIII. The calculated E values for CR and AB210 were 11.53 and 19.50 KJ/mol, respectively. These results showed that the chemisorption phenomenon is operative for adsorption of CR and AB210 in aqueous binary mixture onto BIII.

3.4. Adsorption thermodynamics analysis

Herein, adsorption thermodynamic of a system is employed to investigate the feasibility and spontaneity of it. The change in Gibb's free energy, enthalpy, and entropy associated with adsorption of CR and AB210 in aqueous binary mixture onto AEM BIII were calculated by employing below equation:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{19}$$

$$K_c = \frac{C_a}{C_e} \tag{20}$$

$$\Delta G = \Delta H - T\Delta S \tag{21}$$

where K_c represents the equilibrium constant, C_a denotes the amount of dye (mol/L) adsorbed on the adsorbent per liter (L) of the solution at equilibrium, C_e shows equilibrium concentration (mol/L) of dye in solution, R represents the general gas constant (8.31 J/mol K), and T shows absolute temperature (K). Similarly, $\Delta G°$ represents the change in Gibb's free energy (KJ/mol), $\Delta H°$ shows the change in enthalpy (KJ/mol), and $\Delta S°$ shows the change in entropy (J/mol K). Fig. 7 depicts plot of $\ln(K_c)$ vs. $1/T$ for adsorption of CR and AB210 in aqueous binary mixture onto AEM BIII. The change in enthalpy ($\Delta H°$) and entropy ($\Delta S°$) can be determined from slope and intercept of Fig. 7 and are given in Table 5. The negative values of D$G°$ showed that adsorption of CR and AB210 in binary mixture onto AEM BIII was spontaneous in nature. The positive values of enthalpy showed that adsorption of CR and AB210 in binary mixture onto AEM is an endothermic process. Similarly, the positive values of $\Delta S°$ represent the increase in randomness at the adsorbent–adsorbate interface during the CR and AB210 adsorption onto BIII.

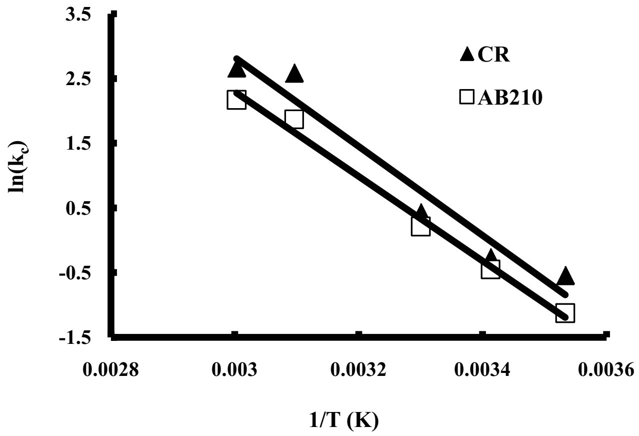


Fig. 7. Plot of $1/T$ vs. $\ln(K_c)$ for adsorption of CR and AB210 onto anion exchange membrane BIII.

3.5. Desorption study

The recycling of adsorbent (AEM BIII) is very crucial for the practical application. Herein, the adsorbent was regenerated by immersing the loaded AEM BIII into 0.001 M HNO_3 solution for 120 min at room temperature. The percentage removal of CR and AB210 was 92.08% and 88.58% in first cycle, respectively. After repeating the cycle, the percentage removal of CR and AB210 was increased up to 96.4% and 95.29% respectively as represented in Fig. 8.

3.6. Environmental applications

The simultaneous removal of CR and AB210 was performed in tap water sample using batch technique in order to investigate the environmental applications of AEM BIII. The tap water was taken from the chemistry department, GSCWU, Bahawalpur, Pakistan. A stock solution of these dyes was prepared in tap water and required concentration was obtained by further dilution. An optimum weight of AEM BIII (0.2 g) immersed in 30 mL of binary mixture of CR and AB210 was taken in culture tubes and placed on orbital shaker. After shaking the absorbance of supernatant was determined and it was noted that adsorption of CR and AB210 was 92.03% and 92% respectively as shown in Fig. 9.

Table 5
Thermodynamic parameters for adsorption of CR and AB210 in aqueous binary mixture onto anion exchange membrane BIII.

Dye	T (K)	$\Delta G°$ (KJ/mol)	$\Delta H°$ (KJ/mol)	$\Delta S°$ (J/mol/K)
Congo Red	283	–1.00317	57.26683	0.195296
	293	–1.16117		
	303	–2.12118		
	313	–4.08117		
	323	–6.04118		
	333	–8.0012		
Acid Black 210	283	–1.89168	54.36525	0.198788
	293	–3.87956		
	303	–5.86744		
	313	–7.85532		
	323	–9.84319		
	333	–11.8311		

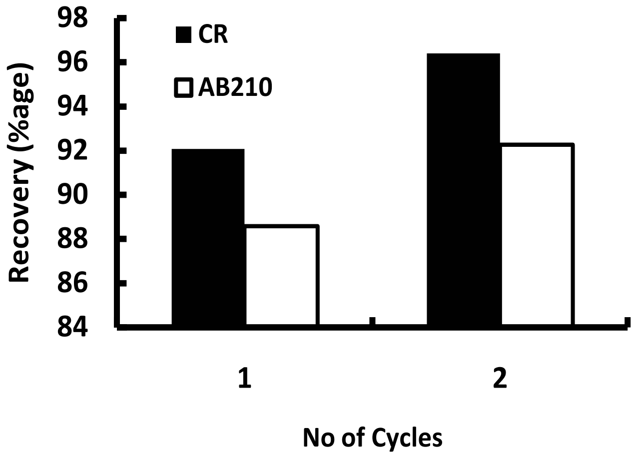


Fig. 8. Percentage desorption of CR and AB210 dyes at different cycles.

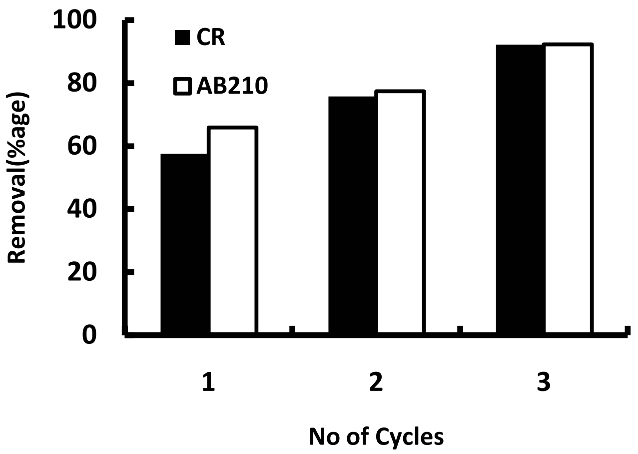


Fig. 9. Percentage removal of CR and AB210 dyes onto anion exchange membrane BIII.

4. Conclusions

In summary, the potential of AEM BIII for adsorption of CR and AB210 in the binary system has been investigated via batch mode. The percentage removal of CR and AB210 in the binary mixture was increased with the contact time, membrane dosage, and temperature whereas decreased with initial dye concentration. Adsorption kinetics study revealed that adsorption of CR and AB210 in binary mixture onto AEM BIII was fitted well to pseudo-first-order kinetic model. Adsorption isotherm investigations showed that adsorption of CR and AB210 in aqueous binary mixture onto AEM BIII obeyed the Langmuir isotherm model. Adsorption thermodynamic study showed that adsorption of CR and AB210 in binary mixture onto AEM was an endothermic process. The percentage desorption of CR and AB210 was 96.4% and 95.29%, respectively while the environmental applicability of CR and AB210 was found out to be 92.03% and 92%, respectively. Therefore, the AEM BIII could be employed for adsorptive removal of CR and AB210 in aqueous binary at ambient temperature.

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