Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.25864

194 (2020) 290–301
August

Adsorptive removal of methyl orange and acid blue-2445 from binary system by anion exchange membrane BI: non-linear and linear form of isotherms

Farzana Hanif[a], Samreen Ehsan[a], Shagufta Zafar[a], Mehwish Akhtar[a], Muhammad Imran Khan[b,*], Muhammad Farooq Warsi[c], Shamroza Mubarik[a], Warda Hassan[d], Imran Shakir[e], Suryyia Manzoor[f,*]

[a]*Department of Chemistry, The Government Sadiq College Women University, Bahawalpur, 63100 Pakistan, Tel. 00923017745540; email: farzanawajid67@gmail.com (F. Hanif), Tel. 00923065099572; email: samreenehsan567@gmail.com (S. Ehsan), Tel. 00923042169536; email: shg_zf@gscwu.edu.pk (S. Zafar), Tel. 00923245184540; email: mehwish.akhtar@gscwu.edu.pk (M. Akhtar), Tel. 00923227666144; email: Shamroza.mubarik@gscwu.edu.pk (S. Mubarik)*
[b]*School of Energy and Power Engineering, Xi'an Jiaotong University, 28 West Xianning Road, Xi'an 710049, Shaanxi, PR. China, Tel. 008615256975744; email: raoimranishaq@gmail.com (M. Imran Khan)*
[c]*Department of Chemistry, Baghdad-ul-Jadeed Campus, The Islamia University of Bahawalpur, 63100 Pakistan, Tel. 00923006342261; email: farooq.warsi@iub.edu.pk (M.F. Warsi)*
[d]*Department of Chemistry, The Women University Multan, Multan P.O. Box: 60000, Pakistan, Tel. 00923336555542; email: warda.chem@wum.edu.pk*
[e]*Sustainable Energy Technologies Center, College of Engineering, King Saud University, P.O. Box: 800, Riyadh 11421, Saudi Arabia, Tel. 00966533867920; email: mshakir@ksu.edu.sa (I. Shakir)*
[f]*Institute of Chemical Sciences, Bahauddin Zakariya University, Bosan Road, Multan, Pakistan, Tel. 00923484138516; email: suryyia878@gmail.com (S. Manzoor)*

Received 17 October 2019; Accepted 20 March 2020

ABSTRACT

In this article, batch adsorption of methyl orange and acid blue-2445 from the binary system onto the anion exchange membrane (BI) was studied at room temperature. The effect of endowment including membrane dosage, contact time, and initial concentration on the percentage removal of dye was investigated. The percentage of dye removal increased with the increase in contact time and reached a maximum after 2 h. The optimum membrane dosage for removal of these anionic dyes was found to be 0.3 g with the rise of temperature from 283–323 K. Experimental results were subjected to non-linear and linear forms of several isotherms such as Freundlich, Langmuir, Temkin, Dubinin–Radushkevich, Harkin's–Jura, Halsey, Flory–Huggins, Hill, Toth, Sips, and Redlich–Peterson isotherms. The Langmuir adsorption capacity was computed from a linear and non-linear form of isotherms. The thermodynamic parameters indicated that the adsorption of methyl orange and acid blue-2445 is both thermodynamically spontaneous in nature. The positive value of enthalpy changes exhibited endothermic nature for the adsorption of methyl orange and acid blue-2445 on anion exchange membrane BI. These results showed that anion exchange membrane BI could be used for wastewater management.

Keywords: Binary system; Anion exchange membranes; Adsorption; Methyl orange; Isotherm

* Corresponding authors.

1. Introduction

The rapid increase in population pressure and consequently tremendously growing industries have changed the environmental conditions throughout the world. These changes have very harmful effects on human beings and other living organisms [1]. The presence of poisonous chemicals in industrial effluent poses a serious health problem to humans, animals, and other aquatic life, and color is the first pollutant to be recognized in the industrial wastewater [2,3]. Paper, plastic and dying industries are using an enormous amount of colors to dye their product consequently dyes containing wastewater generated from these industries are a powerful source for inducing pollution in the aquatic environment [4,5]. Dyes can be detected by the human eye even at a concentration of less than 1 mg L^{-1} due to its intense color. Annual production of dyes throughout the world is 7×10^5 tons of which $1–1.5 \times 10^5$ is discharged into the environment in the wastewater. The largest proportion of dyes about 36,000 ton y^{-1} is consumed by the textile industry resulting in industrial wastewater comprises over 10%–20% of these dyes [6]. The well-known reported sources of dyes are the textile industry, paper, paint, leather, and pigment industries [4,7]. The dyes contain aromatic groups are noxious and carcinogenic and inflict human seriously. They pose serious problems to aquatic life because a minute quantity of dyes in water can severely alter its salinity, observable change in coloration, diminish the perforation of light thus retarding the rate of photosynthesis [8]. The most commonly used dyes are methyl orange, crystal violet, and acid blue, etc. The prolonged exposure of these dyes can cause various disorders in human beings including jaundice, hypersensitivity, migraines, nausea, dizziness, and breathing difficulty [9]. Methyl orange azo dyes are extensively used in the textile industry and different chemical experiments. Besides its numerous applications in industries and research, methyl orange solution is toxic and can cause skin irritation. This is due to its structural stability and low degradability in the environment [10,11]. Moreover, it has also shown detrimental effects on human beings, aquatic life, and another animal too [12]. These dark aspects of dyes have led to tremendous pressure for its separation and purification. Several remediation technologies are available for their safe removal from wastewater. These technologies are summarized as precipitation microbial degradation, chemical oxidation photolysis, and adsorption, ion exchange, precipitation, membrane separation concentration, solvent extraction, reverse osmosis, evaporation, coagulation, electrochemical reduction, coagulation, photocatalytic reduction, and electrodialysis [13]. Although these methods have been widely applied for dye removal there are still several limitations in the application of these methods such as high cost. Hence, these drawbacks rendered them as uneconomical due to huge energy consumption, generation of insanitary materials, deadly poisoned slurry formation, and their scarcity in nature [14–16].

Adsorption process has attained numerous advantages than other conventional techniques for dye removal. Most of the outstanding features of the adsorption process are low price, remarkable selectivity, and the extraordinary property of possible recycling [17]. Various industrial, agricultural, natural or biological materials have the ability to adsorb different dyes and can be used as adsorbents, for example, fly ash rice husk, corn cobs, wheat bran, sawdust, peat, wood, pine bark, banana pith, cottonseed hulls, sawdust, orange peel, etc. [18]. In these numerous adsorbents, anion exchange membranes and resins are evaluated as efficient adsorbents for decolorization of wastewater. However, ion exchange resins have a porous structure but have issues in packed bed operations such as sluggish diffusion, low flow speed, the decline in pressure, irregular, and inconsistent packing. The application of the ion exchange membrane can effectively remove all these above-stated problems of ion exchange resins. Thus anion exchange membrane becomes an attractive choice for the treatment of industrial wastewaters [19].

The main goal of the present work is to evaluate the adsorption capacity of methyl orange and acid blue-2445 by the implementation of anion exchange membrane B1 as adsorbent. The effects of several parameters, for instance, initial dye concentration, adsorbent dosage, and contact time were evaluated for the adsorption of both dyes from dyes mixture. Four different kinetic models including pseudo-first-order, pseudo-second-order, modified Freundlich equation, and Elovich models were applied to experimental data and kinetic parameters were interpreted. Different isotherms like Langmuir, Temkin, Freundlich, Dubinin–Radushkevich, Flory–Huggins, Harkin's–Jura, Hill, Sips, and Redlich–Peterson were also applied [20].

2. Experimental setup

2.1. Adsorbate

The commercially available well-known methyl orange, an anionic dye (MF: $C_{14}H_{14}N_3NaO_3S$, λ_{max}: 464 nm) was obtained from Sigma-Aldrich (St. Louis, Missouri) and used as adsorbent. The acid blue-2445 dye is a member of anthraquinone class and this acidic dye is mostly used dye in industries after azo dyes. It was also purchased from Sigma-Aldrich (St. Louis, Missouri). The stock solution of each dye was prepared by dissolving 1.0 g of it in 1 L of double distilled water and other required concentrations of these dyes were prepared by further dilution of the stock solution. All chemicals used to perform experiments in this research were of analytical grade.

2.2. Adsorbent

The commercially available anion exchange membrane BI provided by ChemJoy Membrane Co. Ltd., (Anhui, Hefei, China) was employed as an adsorbent. It was manufactured with the blends of polyvinyl alcohol and quaternized poly(2,6-dimethyl-1,4-phenylene oxide) [21]. This membrane was exploited without any treatment. The water uptake and ion exchange capacity of the BI membrane are 42.7% and 0.55 mmol g^{-1} [21].

2.3. Adsorption experiment

Adsorption experiments were performed using a batch method as reported in our previous work [22–24]. In a typical experiment, batch adsorptions of dyes were done by

submerging a known amount of adsorbent BI in 40 mL of known concentration of dye solutions. After that, flasks were shaken with 120 rpm speed. At a predetermined time, the flasks were removed from the shaker, and then the residual dye concentration was measured with the help of a UV/VIS spectrophotometer (Agilent Technologies Cary 60 UV-Visible) by recording the absorbance of the supernatant at its lambda maximum. While the concentration of each dye in the reaction mixture was determined with the help of the calibration curve. Adsorption tests were accompanied by varying membrane dose, initial dye concentration, contact time, and different adsorption kinetics, isotherms and thermodynamic parameters were calculated under optimal conditions. The adsorption of selected dyes onto the BI membrane at time t was determined by Eq. (1).

$$q_t = \frac{C_0 - C_t}{W} \times V \tag{1}$$

where C_0 and C_t are the initial and final (at any time t) concentrations of dyes, respectively, and W and V are the weight of adsorbent and volume of dyes solution.

2.4. Characterization

Fourier-transform infrared (FTIR) spectra were obtained before and after the adsorption of dyes on the membrane BI using the Bruker Alpha II FTIR spectrophotometer. The scan was recorded between 4,000 cm^{-1} and 650 cm^{-1}.

3. Results and discussion

3.1. FTIR studies

FTIR analysis is utilized to identify the number of peaks that represent the structure of the anion exchange membrane BI. Fig. 1 represents the FTIR spectra of anion exchange membranes BI before and after adsorption of both dyes namely methyl orange and acid blue-2445. Before adsorption, the band appeared in a range of 2,750–3,050 cm^{-1} is due to $-CH_3$ stretching of poly(2,6-dimethyl-1,4-phenylene oxide) backbone of anion exchange membrane BI while the peaks in the range of 3,070–3,350 cm^{-1} is owing to the presence of –OH groups in the membrane. The band observed in the region of 1,600–1,620 cm^{-1} is related to C–N group stretching vibrations. After adsorption of dyes, slight changes in peaks are observed in the spectra as shown in Fig. 1. This can be attributed to the interaction of methyl orange and acid blue-2445 dyes and the anion exchange membrane BI. The C–N stretching band observed at lower frequencies in contrast with the position before the adsorption. Moreover, the increased peak intensity of the C–N group has also supported the adsorption of dyes on membrane BI. An additional peak appeared in the range 1,345 cm^{-1} is due to the –S=O group starching vibrations demonstrating the successful adsorption of dyes on the membrane surface BI. Hence, these results indicated the successful adsorption of both dyes onto anion exchange membrane BI.

In this work, as we reported the effective removal of the dyes methyl orange and acid blue-2445, which are anionic in nature and the membrane BI is an anion exchange membrane. Fig. 2 describes the proposed mechanism.

3.2. Effect of operating factors

The influence of operational factors such as contact time, adsorbent dosage, initial dye concentration, and temperature on the removal of methyl orange and acid blue-2445 from dyes mixture has been examined. Their detail is given below.

3.2.1. Effect of contact time

The performance of the adsorption process was greatly affected by the contact time. The influence of contact time

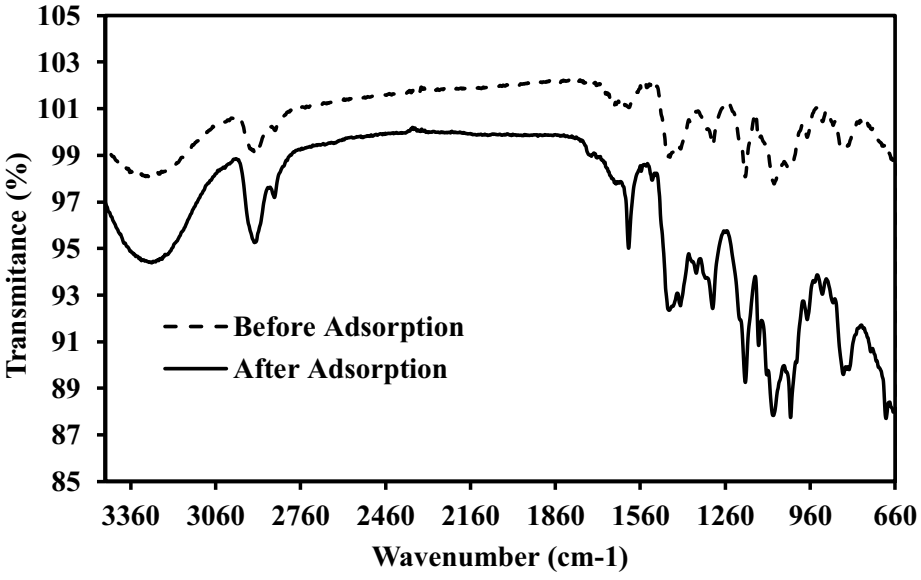

Fig. 1. FTIR spectra of anion exchange membranes BI before and after adsorption of methyl orange and acid blue-2445.

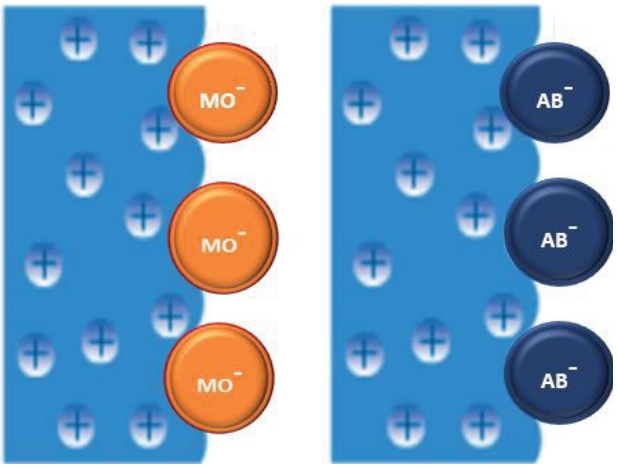

Fig. 2. Mechanism of dyes adsorption on anion exchange membranes.

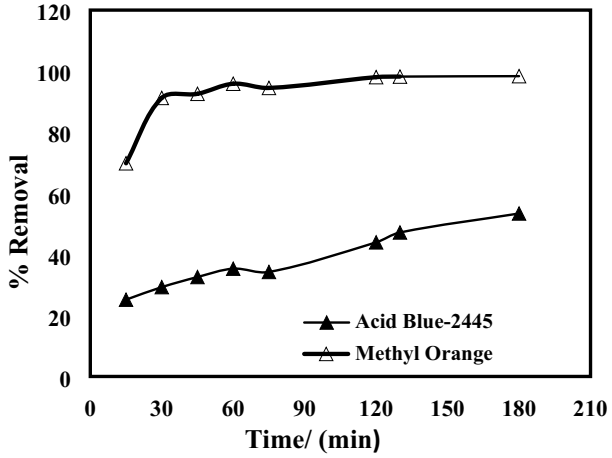

Fig. 3. Effect of contact time on the removal of methyl orange and acid blue-2445 from a binary system.

onto the adsorption capacity was examined at normal room temperature keeping the concentration of methyl orange dye (100 mg L^{-1}) and acid blue-2445 (25 mg L^{-1}) and by keeping the adsorbent dose constant (0.1 g) and the obtained results are shown in Fig. 3. These results revealed that adsorption of both dyes on anion exchange membrane BI enhanced with raising in contact time. After 2 h, the maximum adsorption of methyl orange and acid blue-2445 on the surface of the anion exchange membrane was attained and after this stage the adsorption was insignificant. The rate of adsorption capacity is higher in the initial stage because at this stage all the reaction sites were empty therefore the rate of percentage removal was high in the beginning. With the passage of time, most of the number of accessible active sites on adsorbent surface decreased due to saturation of dyes molecules on these sites and owing to the repulsive forces between the bulk phase and solute molecules in solid.

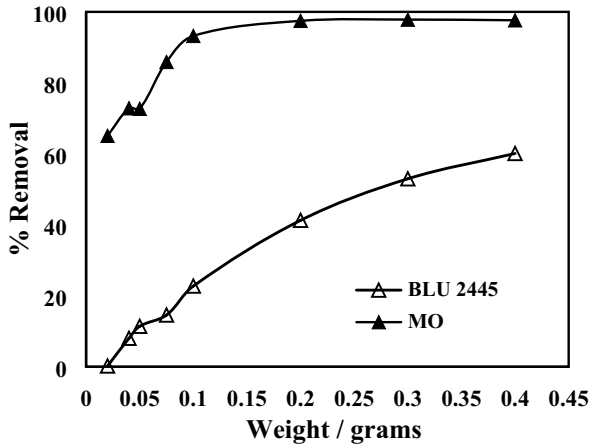

Fig. 4. Effect of membrane dosage on the removal of methyl orange and acid blue-2445 from a binary system.

3.2.2. Effect of membrane dosage

Adsorbent mass is a key parameter that plays a critical role in adsorption. To observe the minimal amount which yields maximum adsorption, the effect of anionic membrane dose on simultaneous removal of methyl orange and acid blue-2445 was investigated by keeping all other experimental conditions constant. When the adsorbent dose enhanced from 0.02 to 0.3 g the adsorption of dyes increased. At 0.3 g, the removal of methyl orange and acid blue-2445 was as high as 97.82% and 52.96%, respectively. Obviously with the elevation of the amount of adsorbent the adsorption sites for dyes increased. The results of experiments revealed that 0.3 g is the optimum membrane dosage for decontamination of methyl orange and acid blue-2445 from the binary system as shown in Fig. 4.

3.2.3. Effect of initial dye concentration

The initial dye concentration has a prominent effect on the adsorption capacity of the membrane. The influence of initial dye concentration on the adsorption capacity of methyl orange and acid blue-2445 on BI was revealed by using the adsorbent dose 0.3 g and contact time of 2 h at room temperature and results are shown in Fig. 5. These results indicated that the interaction becomes strong between adsorbate and adsorbent with an elevation of initial dye concentration. It was recorded that the removal efficiency of methyl orange decrease from 99% to 97% and 97% to 35% when initial concentration was increased from 50 to 150 mg L^{-1} and 5 to 50 mg L^{-1} for methyl orange and acid blue-2445 respectively. The higher adsorption capacity was detected at a low concentration which is due to the availability of excess sorption sites. The lower adsorption capacity at higher concentrations was attributed to saturation of active sites as well as possible repulsive forces between dyes ions and dyes molecules adsorbed on the adsorbent surface.

3.3. Adsorption isotherms

Adsorption isotherms furnish valuable description about the adsorption potential of the adsorbents and type of adsorbent–adsorbate interaction. These isotherms explain

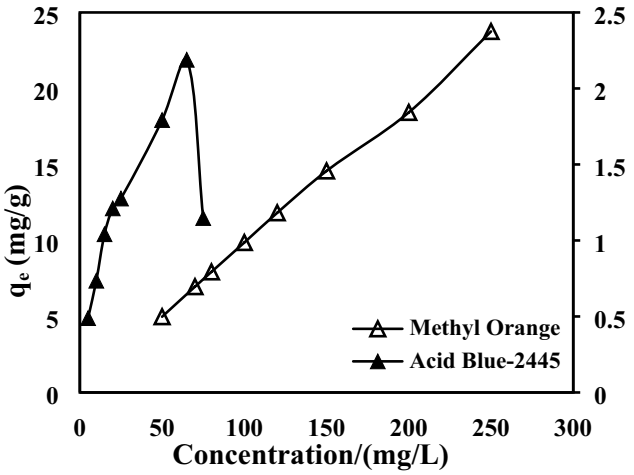

Fig. 5. Effect of initial dye concentration on the adsorption capacity of methyl orange and acid blue-2445.

the interdependence between the number of dyes adsorbed on the adsorbent and the equilibrium concentration of the adsorbate. The study of isotherm data by applying different isotherm models provides information about the appropriate model which can be applied to explain the adsorption procedure. There is a number of adsorption isotherms that can be employed for the comprehensive explanation of the adsorption process.

3.3.1. Non-linear isotherms

The non-linear form of Langmuir isotherm can be stated as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

where K_L is Langmuir constant, q_m is the adsorption capacity. The non-linear model for Langmuir isotherm is represented in Figs. 6a and b. The value of K_L and q_m are represented in Table 1. The value of chi-square for methyl orange and acid blue-2445 is 0.652 and 0.043, respectively. The non-linear form of Freundlich isotherm can be stated as:

$$q_e = K_f C_e^{1/n} \tag{3}$$

where C_e is the equilibrium concentration at equilibrium stage, q_e is the adsorbed dye's amount at equilibrium, n and K_f are Freundlich parameters its values are given in Table 1. The value of chi-square for adsorption of methyl orange and acid blue-2445 is 4.47 and 0.29, respectively.

The non-linear Temkin isotherm can be expressed as:

$$q_e = \frac{RT}{b_T \ln\left(a_T C_e\right)} \tag{4}$$

where R, T, b_T, and a_T constants refer to universal gas constant (8.31 J mol K^{-1}), absolute temperature (K), the heat of

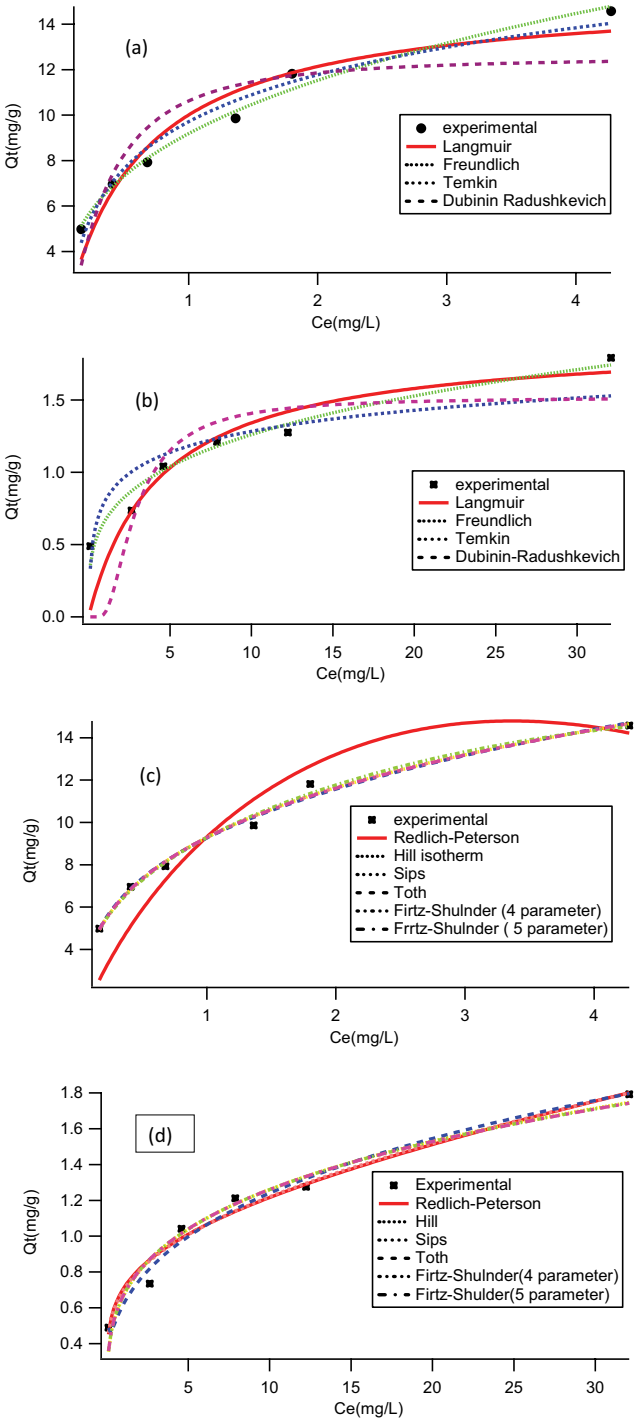

Fig. 6. Non-linear plots of Langmuir, Freundlich, Temkin, and Dubinin–Redushkevich isotherms for the adsorption of (a) methyl orange, (b) acid blue-2445, and non-linear plots of Redlich–Peterson, Hill, Sips, Toth, Fritz–Schlunder and Frotz–Sch for the adsorption of (c) methyl orange and (d) acid blue-2445.

adsorption, and equilibrium binding constant corresponding to maximum binding energy, respectively. The non-linear plot of Temkin isotherm is presented in Figs. 6a and b. The value of a_T and b_T constants are calculated and given

Table 1
Linear and non-linear isotherms parameters for adsorption of methyl orange and acid blue-2445 on anion exchange membrane BI

System	Methyl orange		Acid blue-2445	
Langmuir isotherm				
	Non-linear form		Linear form	
	Methyl orange	Acid blue-2445	Methyl orange	Acid blue-2445
q_m (mg g^{-1})	15.432	1.921	17.24	2.06
K_L (L mg^{-1})	1.843	0.231	1.28	0.18
R_L	–	–	0.007	0.18
R^2	–	–	0.991	0.989
χ^2	4.477	0.229	–	–
Freundlich isotherm				
	Non-linear form		Linear form	
	Methyl orange	Acid blue-2445	Methyl orange	Acid blue-2445
K (L mg^{-1})	9.187	0.664	2.62	0.78
N	3.051	3.598	3.06	3.07
R^2	–	–	0.985	0.955
χ^2	0.652	0.043	–	–
Temkin isotherm				
	Non-linear form		Linear form	
	Methyl orange	Acid blue-2445	Methyl orange	Acid blue-2445
β (mg L^{-1})	0.822	11.677	3.347	0.4
α (L mg^{-1})	25.981	45.096	475.32	0.96
R^2	–	–	0.976	0.974
χ^2	1.7621	0.175	–	–
Dubinin–Radushkevich isotherm				
	Non-linear form		Linear form	
	Methyl orange	Acid blue-2445	Methyl orange	Acid blue-2445
B	0.084	1.331	0.057	1.519
E	2.4	0.61	–	–
q_m (mg g^{-1})	12.8	1.46	12.555	1.391
R^2	0.842	0.842	0.842	0.9686
χ^2	–	–	11.96	0.378
Harkin's–Jura isotherm				
	Linear form			
	Methyl orange		Acid blue-2445	
B	0.8066		0.79	
A	62.5		1.609	
R^2	0.949		0.795	
Halsey isotherm				
	Linear form			
	Methyl orange		Acid blue-2445	
n_H	3.08		3.012	
k_H	912		0.491	
R^2	0.985		0.955	

Flory–Huggins isotherm		
Linear form		
	Methyl orange	Acid blue-2445
n_{fH}	–0.011	–0.158
K_{fH}	0.97	0.93
R^2	0.963	0.92
Redlich–Peterson isotherm		
Non-linear form		
	Methyl orange	Acid blue-2445
K	36.6	0.014
A	27.29	0.689
G	1.136	0.191
χ^2	12.14	0.027
Hill isotherm		
Non-linear form		
	Methyl orange	Acid blue-2445
q_H	50.81	8814.4
n_H	0.409	0.28
K_d	4.46	13331
χ^2	0.569	0.043
Sips isotherm		
Non-linear form		
	Methyl orange	Acid blue-2445
k_s	11.36	0.321
B	0.409	0.096
a_s	0.223	0.535
χ^2	0.569	0.0256
Toth isotherm		
Non-linear form		
	Methyl orange	Acid blue-2445
k_T	9.4	0.591
a_T	0.022	0.057
T	1.44	1.47
χ^2	0.609	0.0178
Fritz–Schlunder		
Non-linear form		
	Methyl orange	Acid blue-2445
A	4,629.2	8.5329
A	2.107	0.28
B	497.4	11.83
B	2.462	0.00273
χ^2	0.499	0.043

(Continued)

Table 1 Continued

Frotz–Sch		
Non-linear form		
	Methyl orange	Acid blue-2445
Q	119.56	33.331
k_1	0.123	0.034
m_1	0.214	0.277
k_2	0.587	0.721
m_2	0.316	0.00047
χ^2	0.582	0.043

in Table 1. The value of chi-square for Temkin isotherm for methyl orange and acid blue-2445 are 1.7621 and 0.175, respectively.

The non-linear form of Dubinin–Redushkevich (D–R) can be expressed as:

$$q_e = C_m \exp\left(-\beta\varepsilon^2\right) \tag{5}$$

The non-linear plot of D–R is given in Figs. 6a and b. The value of chi-square for the adsorption of methyl orange and acid blue-2445 is 11.96 and 0.378, respectively.

The non-linear form of Redlich–Peterson can be expressed as:

$$q_e = \frac{K_{\mathrm{R-P}} C_e}{1 + a_{\mathrm{R-P}} C_e^{\,g}} \tag{6}$$

The R–P chi-square value for adsorption of methyl orange and acid blue-2445 comes out to be 12.14 and 0.027, respectively. The parameters for R–P recorded are listed in Table 1 and a non-linear plot for this graph is represented in Figs. 6c and d.

Sips isotherm is also a hybrid form of both Freundlich and Langmuir isotherm. This model is well-suited for the description of adsorption on the heterogeneous surface. The expression of a non-linear form of Sips isotherm is given as:

$$q_e = \frac{k_s C_e^{\,\beta_s}}{1 + a_s C_e^{\,\beta_s}} \tag{7}$$

At low concentration, Sips isotherm converted into Freundlich isotherm and at high concentration, it obeys Langmuir isotherm [25]. The description of Sips parameters is provided in Table 1 and a non-linear plot for this graph is represented in Figs. 6c and d.

The non-linear form of Hill isotherm can be stated as:

$$q_e = \frac{q_H C_e^{n_H}}{k_H} + C_e^{n_H} \tag{8}$$

The plot for the Hill model is expressed in Figs. 6c and d and calculated constants are shown in Table 1.

The Toth isotherm is the modified form of the Langmuir equation. This model is applied for the description of the heterogeneous system including both low and high boundary of adsorbate concentration. The values of Toth isotherm can be obtained by using the non-linear form which can be expressed as:

$$q_e = \frac{k_T C_e}{\left(a_T + C_e\right)^{1/t}} \tag{9}$$

The description of Toth parameters is provided in Table 1 and a non-linear plot for this graph is represented in Figs. 6c and d.

3.3.2. Linear isotherms

The Langmuir isotherm is normally applied to examine the monolayer adsorption on the homogeneous surface of the adsorbent. This empirical model suggests adsorption may take place on a specified number of indistinguishable and comparable fixed sites with no lateral communication and steric impairment even at adjoining sites. The Langmuir adsorption isotherm suggests the homogeneous adsorption of molecules onto a solid surface with constant sorption activation energies and enthalpies of each molecule. All sites have the same attraction for adsorbate. The linear form of this isotherm can be expressed as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \tag{10}$$

Here, K_L (L mg^{-1}) and q_m (mg L^{-1}) are the Langmuir constants while C_e (mg L^{-1}) and q_e (mg L^{-1}) are the dye concentration in solution at equilibrium and adsorbed adsorbate amount at equilibrium [26]. A plot of C_e/q_e vs. q_e for a linearized form of Langmuir isotherm yields a straight line as shown in Fig. 7a and values of parameter K_L and q_m are determined from the slope and intercept of the graph as listed in Table 1. The important properties of the Langmuir equation can be indicated in the form of dimensionless separation factor R_L that can be well-defined as:

$$R_L = \frac{1}{\left(1 + bC_0\right)} \tag{11}$$

where C_0 is the maximum initial concentration of a solution (mg L^{-1}) and b stands for Langmuir isotherm constant

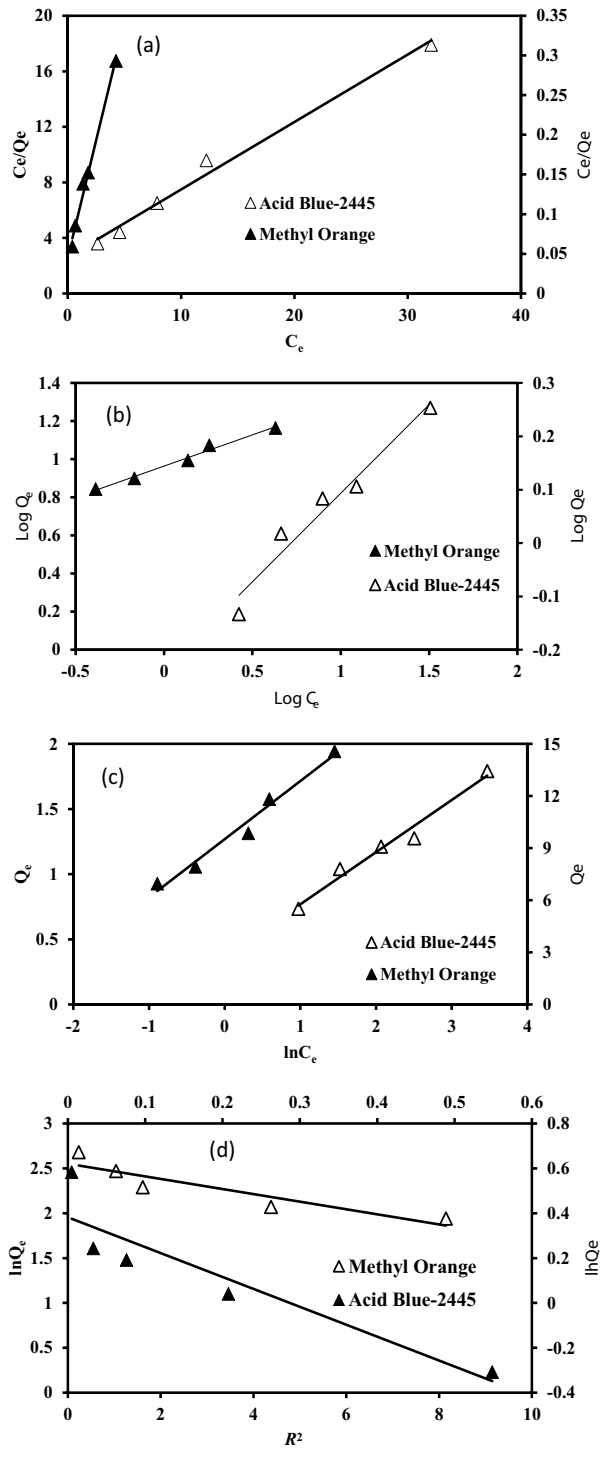

Fig. 7. The linear form of (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) Dubinin–Redushkevich isotherm for the adsorption of methyl orange and acid blue-2445 from the binary system onto BI.

(L mg^{-1}). The R_L value represented the adsorption is unfavourable for $R_L > 1$, linear for $R_L = 1$, irreversible for $R_L = 0$ and favourable between $0 < R_L < 1$. According to Table 1, the R_L values for methyl orange were 0.007 and for acid blue-2445 was 0.18 which confirmed that anion exchange membrane BI is a favorable adsorbent for adsorption of both anionic dyes from the binary mixture under optimal experimental conditions. The value of the R^2 value of methyl orange and acid blue-2445 comes out to be 0.991 and 0.989, respectively which indicated the feasibility of the functionality of the Langmuir model for binary adsorption of methyl orange and acid blue-2445.

Freundlich isotherm can be derived by supposing a logarithmic decrease in the enthalpy of adsorption, with the elevation of fractional occupied sites. This isotherm is a well-known model that describes non-ideal as well as reversible adsorption not confined to the monolayer formulation. According to this model, the adsorption at all sites gives the amount of adsorbed dye. Firstly, the accumulation of adsorbate molecules occurs at stronger sites till the adsorption energy is exponentially reduced after the adsorption process is completed. The logarithmic form of this isotherm can be represented as:

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{12}$$

where n and K_f and are Freundlich constants. The constant K_f (mg$^{1-1/n}$ L$^{1/n}$ g) shows the relative adsorption capacity of the adsorbent and n gives an idea about the favorable adsorption process. The graph logq_e vs. logC_e for the linear equation of Freundlich isotherm yields a straight line as shown in Fig. 7b. The slope 1/n ranging from 0–1 delivers information about the heterogeneity of the surface. The heterogeneity of the surface-enhanced when the value of 1/n becomes closer to zero. Freundlich constant K_f and n are measured and listed in Table 1. The recoded value of 1/n for methyl orange and acid blue-2445 was 0.326 and 0.238, respectively which indicated the heterogeneity of surface. The correlation coefficient factor R^2 was 0.985 for methyl orange and 0.955 for acid blue-2445. These results revealed the high applicability of the Freundlich isotherm model for experimental data of both methyl orange and acid blue-2445.

According to Temkin isotherm, there is a linear decrease in heat of adsorption by increasing coverage. The linear form of Temkin isotherm can be stated as [27]:

$$q_e = \beta \ln A + \beta \ln C \tag{13}$$

$$B = \frac{RT}{b} \tag{14}$$

The plot of lnC_e vs. q_e for a linearized form of Temkin isotherm gives a straight line as presented in Fig. 7c. The value of R^2 was 0.976 and 0.974 for methyl orange and acid blue-2445, respectively. The high values of R^2 show the applicability of Temkin isotherm for binary adsorption of methyl orange and acid blue-2445.

D–R describes the apparent energy of adsorption. The linear form of the D–R model can be stated as [28]:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{15}$$

$$\varepsilon = RT\ \ln\left(1+\frac{1}{C_e}\right) \tag{16}$$

where q_m (mg g^{-1}) is the maximum sorption capacity, β is activity coefficient constant associated with sorption energy and ε is Polanyi potential. Mean free energy can be calculated as:

$$E = \frac{1}{\sqrt{2\beta}} \tag{17}$$

A graph is plotted between Polanyi potential ε^2 and $\ln q_e$ for a linear form of D–R isotherm as shown in Fig. 7d. The mean free energy delivers information about the nature of adsorption. If the value of E is ranging from 8 to 16 J mol^{-1} then the nature of adsorption will be chemical and if E < 8 J mol^{-1} then the process will be physical in nature. The value of mean free energy was between 2.4 and 0.61 J mol^{-1} which suggested the physical nature of the adsorption. The values of the regression coefficient R^2 was 0.842 for both methyl orange and acid blue-2445.

Harkin's–Jura (H–J) isotherm considers the multilayer adsorption and heterogeneous adsorption of pores. The linearized isotherm model can be stated as:

$$\frac{1}{q_e^2} = \frac{B}{A} - \left(\frac{1}{A}\right)\log C_e \tag{18}$$

where A and B are Harkin's–Jura constants. The values of constants A and B are measured from the slope and intercept of $1/q_e^2$ vs. $\log C_e$ as shown in Fig. 8a. A high value of correlation coefficient R^2 about 0.949 indicated the applicability of this model for methyl orange, while the relatively low value of correlation coefficient about 0.795 represented relatively poor applicability of this model for acid blue-2445.

Halsey suggested an expression for the multilayer condensation at a comparatively greater distance from the surface. This equation provides information about heteroporosity of the adsorbent. The linearized Halsey model can be stated as:

$$\log q_e = \frac{1}{n_H}\log K_H - \frac{1}{n_H}\log C_e \tag{19}$$

The plot of $\log C_e$ vs. $\log q_e$ for linearized Halsey isotherm is indicated in Fig. 8b. The high values of the regression coefficient factor R^2 about 0.985 for methyl orange and 0.955 for acid blue-2445 indicated the heteroporosity of the anion exchange membrane BI.

Flory–Huggins isotherm provides information about the extent of surface coverage of the adsorbate on the adsorbent. The linearized Flory–Huggins isotherm model [29] can be expressed as:

$$\log\frac{\theta}{C_e} = \log\left(K_{\text{fH}}\right) + n_{\text{fH}}\log\left(1-\theta\right) \tag{20}$$

where K_{fH} is Flory–Huggins constant, n_{fH} is the isothermic exponent and θ is the extent of surface coverage. A plot of

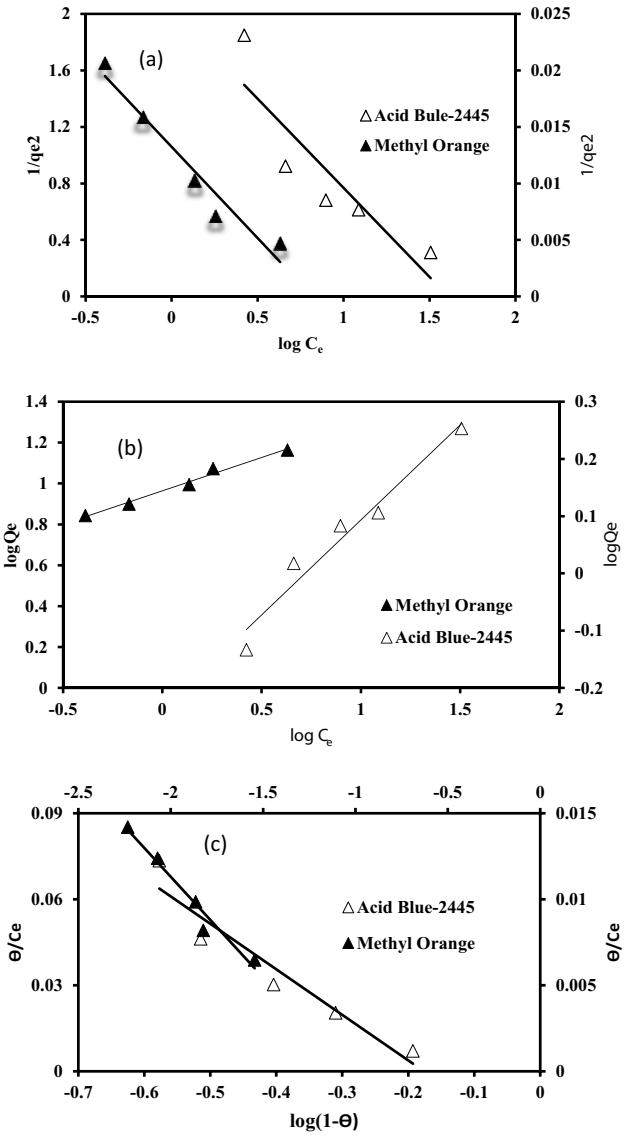

Fig. 8. The linear form of (a) Harkin's–Jura (H–J), (b) Halsey, and (c) Flory–Huggins for adsorption of methyl orange and acid blue-2445 from the binary system onto BI.

log(1–θ) vs. log(θ/C_e) for a linear form of Flory–Huggins isotherm is indicated in Fig. 8c. The value of the correlation coefficient for methyl orange and acid blue-2445 was 0.963 and 0.920, respectively.

3.4. Adsorption thermodynamics

The thermodynamic adsorption parameters namely Gibb's free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) associated with the adsorption of these anionic dyes onto anion exchange membrane B1 were calculated by employing Gibb's free energy and Van't Hoff equation and obtained results are listed in Table 2. The plots of $\ln K_c$ vs. 1/T for these anionic dyes with different initial concentration is given in Fig. 9. It is found that the values of Gibb's free energy are negative for adsorption of anionic dyes

Table 2
Thermodynamic parameters for adsorption of methyl orange and acid blue-2445 on anion exchange membrane BI

Dye	Temperature (K)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1})
Methyl orange	283	–3.8912	54.4068	0.206
	303	–8.108		
	313	–10.078		
	323	–12.38		
Acid blue-2445	283	–0.1	44.247	0.1567
	303	–3.2331		
	313	–4.8371		
	323	–6.3671		

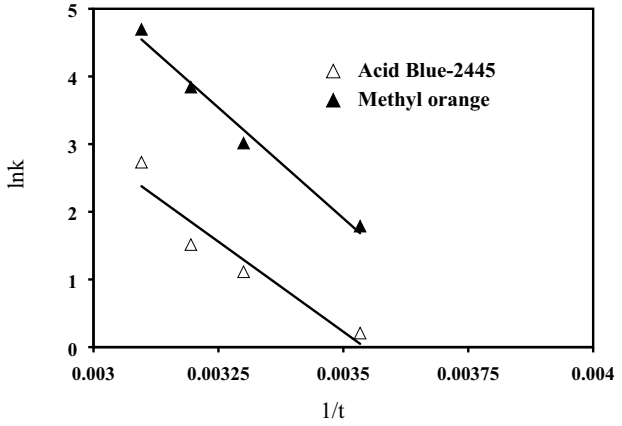

Fig. 9. The plot of 1/T vs. ln$K$ for the adsorption of methyl orange and acid blue-2445 on anion exchange membrane BI.

methyl orange and acid blue-2445 onto the anion exchange membrane and showed an increase in Gibb's free energy ($\Delta G°$) values with the increase of temperature. This can be due to the interaction between the dyes on a solid surface with unequal competition accredited to the heterogeneity of the adsorbent surface and the system attained energy from an external source at high temperatures. The values of enthalpy ($\Delta H°$) are coming out to be positive for both anionic dyes adsorption onto BI indicating the endothermic nature of the adsorption process. Similarly, the values of entropy ($\Delta S°$) for both methyl orange and acid blue-2445 are also positive suggesting the increase in randomness at adsorbent-solution interface during adsorption.

4. Conclusion

As the effective removal of azo dyes is a stringent problem, therefore, in this study, we explored the worth of anion exchange membrane BI for the removal of methyl orange and acid blue-2445 from binary system using the batch system. Several experimental parameters were optimized for maximum dye removal. Experimental results were applied to various isotherms such as Freundlich Langmuir, Temkin, D–R, Harkin's–Jura, Halsey, Flory–Huggins isotherms, Hill, Toth, Sips, Redlich–Peterson. The attained results represented that adsorption of methyl orange and acid blue-2445 onto anion exchange membrane followed linear and non-linear Langmuir isotherm with an adsorption capacity of 15.43 and 17.24 mg g^{-1} for methyl orange by linear and non-linear method respectively whereas for adsorption capacity for acid blue from linear and non-linear plots 1.92 and 2.06 mg g^{-1}. The percentage of dye removal increased with the increase in contact time and reached a maximum after 2 h. The optimum membrane dosage for removal of these anionic dyes was found to be 0.3 g with the rise of temperature from 283–323 K. The thermodynamic parameters showed that the adsorption of methyl orange and acid blue-2445 is both thermodynamically spontaneous in nature. The positive value of enthalpy changes showed endothermic nature for the adsorption of methyl orange and acid blue-2445 on anion exchange membrane. It can be concluded from this study that the anion exchange membrane has the ability to be utilized for wastewater management.

Acknowledgements

The authors would like to thank the Govt. Sadiq College Women University Bahawalpur (Pakistan), The Women University Multan (Pakistan), The Islamia University of Bahawalpur (Pakistan), International Postdoctoral Exchange Fellowship Program (Talent-Introduction Program) and Institute of Chemical Sciences, BZU-Multan. Dr. Imran Shakir sincerely appreciates King Saud University for his contribution through the Researchers Supporting Project (RSP-2019/49).

References

[1] M. Rajabi, K. Mahanpoor, O. Moradi, Removal of dye molecules from aqueous solution by carbon nanotubes and carbon nanotube functional groups: critical review, RSC Adv., 7 (2017) 47083–47090.
[2] J.A. Awomeso, A.M. Taiwo, A.M. Gbadebo, J.A. Adenowo, Studies on the pollution of waterbody by textile industry effluents in Lagos, Nigeria, J. Appl. Sci. Environ. Sanitation, 5 (2010) 353–359.
[3] F. Almomani, R. Bhosale, M. Khraisheh, A. Kumar, T. Almomani, Heavy metal ions removal from industrial wastewater using magnetic nanoparticles (MNP), Appl. Surf. Sci., 506 (2020) 144924.
[4] R. Khan, V. Patel, Z. Khan, Chapter 5 – Bioremediation of Dyes from Textile and Dye Manufacturing Industry Effluent, P. Singh, A. Kumar, A. Borthakur, Eds., Abatement of Environmental Pollutants: Trends and Strategies, Elsevier, Amsterdam, Netherlands, 2020, pp. 107–125.
[5] R.G. Saratale, J.R. Banu, H.-S. Shin, R.N. Bharagava, G.D. Saratale, Textile Industry Wastewaters as Major Sources of Environmental Contamination: Bioremediation Approaches for its Degradation and Detoxification, G. Saxena, R. Bharagava, Eds., Bioremediation of Industrial Waste for Environmental Safety, Springer, Berlin, Germany, 2020, pp. 135–167.
[6] M.H. Ehrampoush, Gh.R. Moussavi, M.T. Ghaneian, S. Rahimi, M. Ahmadian, Removal of methylene blue dye from textile simulated sample using tubular reactor and TiO_2/UV-C photocatalytic process, Iran. J. Environ. Health. Sci. Eng., 8 (2011) 35–40.
[7] M.A. Rauf, S.S. Ashraf, Survey of recent trends in biochemically assisted degradation of dyes, Chem. Eng. J., 209 (2012) 520–530.
[8] V.V. Panić, S.I. Šešlija, A.R. Nešić, S.J. Veličković, Adsorption of azo dyes on polymer materials, Hemijska industrija, 67 (2013) 881–900.

[9] S. Caprarescu, A.R. Miron, V. Purcar, A.-L. Radu, A. Sarbu, D. Ion-Ebrasu, L.-I. Atanase, M. Ghiurea, Efficient removal of Indigo Carmine dye by a separation process, Water Sci. Technol., 74 (2016) 2462–2473.
[10] Y. Tang, R. Yang, D. Ma, B. Zhou, L. Zhu, J. Yang, Removal of methyl orange from aqueous solution by adsorption onto a hydrogel composite, Polym. Polym. Compos., 26 (2018) 161–168.
[11] A.G. Naikwade, M.B. Jagadale, D.P. Kale, A.D. Gophane, K.M. Garadkar, G.S. Rashinkar, Photocatalytic degradation of methyl orange by magnetically retrievable supported ionic liquid phase photocatalyst, ACS Omega, 5 (2020) 131–144.
[12] M. Ismail, S. Gul, M.I. Khan, M.A. Khan, A.M. Asiri, S.B. Khan, *Medicago polymorpha*-mediated antibacterial silver nanoparticles in the reduction of methyl orange, Green Process. Synth., 8 (2019) 118–127.
[13] V. Katheresan, J. Kansedo, S.Y. Lau, Efficiency of various recent wastewater dye removal methods: a review, J. Environ. Chem. Eng., 6 (2018) 4676–4697.
[14] C. Galindo, P. Jacques, A. Kalt, Photodegradation of the aminoazobenzene acid orange 52 by three advanced oxidation processes: UV/H_2O_2, UV/TiO_2 and VIS/TiO_2: comparative mechanistic and kinetic investigations, J. Photochem. Photobiol., A, 130 (2000) 35–47.
[15] M.-C. Lu, Oxidation of chlorophenols with hydrogen peroxide in the presence of goethite, Chemosphere, 40 (2000) 125–130.
[16] A.R. Khataee, V. Vatanpour, A.R.A. Ghadim, Decolorization of C.I. Acid Blue 9 solution by UV/Nano-TiO_2, Fenton, Fenton-like, electro-Fenton and electrocoagulation processes: a comparative study, J. Hazard. Mater., 161 (2009) 1225–1233.
[17] A. Tripathi, M.R. Ranjan, Heavy metal removal from wastewater using low cost adsorbents, J. Biorem. Biodegrad., 6 (2015) 1–5.
[18] X.-s. Wang, Y. Qin, Equilibrium sorption isotherms for of Cu^{2+} on rice bran, Process Biochem., 40 (2005) 677–680.
[19] M.A. Khan, M.I. Khan, S. Zafar, Removal of different anionic dyes from aqueous solution by anion exchange membrane, Membr. Water Treat., 8 (2017) 259–277.
[20] M.I. Khan, T.M. Ansari, S. Zafar, A.R. Buzdar, M.A. Khan, F. Mumtaz, P. Prapamonthon, M. Akhtar, Acid green-25 removal from wastewater by anion exchange membrane: adsorption kinetic and thermodynamic studies, Membr. Water Treat., 9 (2018) 79–85.
[21] M.I. Khan, L. Wu, A.N. Mondal, Z. Yao, L. Ge, T. Xu, Adsorption of methyl orange from aqueous solution on anion exchange membranes: adsorption kinetics and equilibrium, Membr. Water Treat., 7 (2016) 23–38.
[22] M.I. Khan, S. Zafar, M.A. Khan, A.R. Buzdar, P. Prapamonthon, Adsorption kinetic, equilibrium and thermodynamic study for the removal of Congo Red from aqueous solution, Desal. Water Treat., 98 (2017) 294–305.
[23] M.I. Khan, M.A. Khan, S. Zafar, M.N. Ashiq, M. Athar, A.M. Qureshi, M. Arshad, Kinetic, equilibrium and thermodynamic studies for the adsorption of methyl orange using new anion exchange membrane (BII), Desal. Water Treat., 58 (2017) 285–297.
[24] M.I. Khan, S. Akhtar, S. Zafar, A. Shaheen, M.A. Khan, R. Luque, A. ur Rehman, Removal of congo red from aqueous solution by anion exchange membrane (EBTAC): adsorption kinetics and themodynamics, Materials (Basel), 8 (2015) 4147–4161.
[25] A. Roghanizad, M.K. Abdolmaleki, S.M. Ghoreishi, M. Dinari, One-pot synthesis of functionalized mesoporous fibrous silica nanospheres for dye adsorption: isotherm, kinetic, and thermodynamic studies, J. Mol. Liq., 300 (2020) 112367.
[26] A. Dąbrowski, Adsorption—from theory to practice, Adv. Colloid Interface Sci., 93 (2001) 135–224.
[27] S. Khandaker, Y. Toyohara, G.C. Saha, Md.R. Awual, T. Kuba, Development of synthetic zeolites from bio-slag for cesium adsorption: kinetic, isotherm and thermodynamic studies, J. Water Process Eng., 33 (2020) 101055.
[28] D. Ociński, P. Mazur, Highly efficient arsenic sorbent based on residual from water deironing – sorption mechanisms and column studies, J. Hazard. Mater., 382 (2020) 121062.
[29] C. Verma, M.A. Quraishi, E.E. Ebenso, A Review on Ammonia Derivatives as Corrosion Inhibitors for Metals and Alloys, Inamuddin, R. Boddula, A. Asiri, Eds., Sustainable Ammonia Production, Springer, 2020, pp. 49–67.