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Diethylaminoethyl dextran/epichlorohydrin (DEAE-D/ECH) hydrogel as adsorbent for murexide

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ABSTRACT

This study describes the dyestuff removal ability of diethylaminoethyl-dextran–epichlorohydrin (DEAE-D–ECH) polymeric adsorbents. The interaction between DEAE-D–ECH hydrogel and a water-soluble dyestuff, murexide (Mu), was investigated. The effect of different parameters on Mu adsorption efficiency was examined in detail. The equilibrium swelling capacity of DEAE-D hydrogel was determined by swelling in water and dye solution. Scanning electron microscopy micrographs and FTIR spectra, before and after the adsorption of Mu on the hydrogel, were used to explain the adsorption. Additionally, kinetic adsorption ability was well described by the pseudo-second-order kinetic model. The equilibrium data were best described by the Langmuir isotherm model. According to the calculated thermodynamic parameters (ΔG°, ΔH°, and ΔS°), the adsorption process is spontaneous and endothermic.

Keywords: Diethylaminoethyl-dextran–epichlorohydrine hydrogel; Dye adsorption; Murexide; Adsorption kinetic model; Swelling

1. Introduction

Various kinds of synthetic dyestuffs appear in the effluents of wastewater in some industries such as textiles, leather, paper, plastics, etc. [1]. Dyes usually have a synthetic origin and complex aromatic molecular structures, which are more stable and more difficult to biodegrade [2]. As a result, they generate a considerable amount of polluted wastewater [3]. The removal of dyes from aquatic environment is extremely difficult from the point of view of healthiness because most of these dyes are toxic, causing allergy and skin irritation; besides, most of them are mutagenic and/or carcinogenic [4].

During the past decades, several wastewater treatment methods have been reported; coagulation–flocculation [5], activated carbon adsorption [6], oxidation [7], ozoniation [8], electrocoagulation [9], membrane separation [10], biological degradation [11], Fenton reagent [12], ion exchange [13], and irradiation [14] are some examples and they have been attempted for the removal of pollutants from the effluents of textile, pulp, etc.

Adsorption methods are relatively simple, easy to operate and handle, and cost-effective. Dyes can be effectively removed by the adsorption process. It is known different adsorbents have been used for the removal from aqueous solutions of various materials, such as dyes, metal ions, and other organic materials, including silica gels [15], fly ash [16], lignite, peat [17],

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activated carbon [18], natural clays [19], modified clays [20], chitosan [21], cellulose [22], etc. Nowadays, development of new adsorbents which have superior properties, such as high adsorption capacity, fast adsorption rate, and mechanical strength, has generated great interest for wastewater treatment. The use of hydrogels has gained great importance due to their high adsorption capacities [23].

The Murexide (Mu) is an organic compound applied as a complexometric indicator for complexometric titration of the alkali metal ions in some non-aqueous solutions [24]. It was investigated as a promising enhancer of sonochemical destruction of chlorinated hydrocarbon pollutants [25]. According to the former researches since Mu is used in various studies, so during its use, a considerable amount of Mu goes with wastewater to the rivers and oceans and is hazardous for the aquatic lives. Therefore, removal of dye is an important aspect of wastewater treatment before discharge [25,26].

In this study, diethylaminoethyl-dextran–epichlorohydrin (DEAE-D–ECH) hydrogel was prepared, and characterized by scanning electron microscopy (SEM) and FTIR. The adsorption equilibrium of Mu dye onto DEAE-D–ECH hydrogel from aqueous solution was investigated in detail. The Langmuir and Freundlich equations were used to fit the isotherm equilibrium. Thermodynamic parameters were also calculated. The kinetic adsorption of Mu on the DEAE-D–ECH hydrogel was determined with three different kinetic models: the pseudo-first-order, the pseudo-second-order, and the intraparticle diffusion model. In addition, various thermodynamic parameters, such as standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°), standard entropy (ΔS°), and the activation energy (E_a), were calculated. This information will be useful for further applications of system design in the treatment of practical waste effluents.

2. Materials and methods

2.1. Materials

DEAE-D chloride [Mw: 500,000 g/mol] used in this study was supplied by Sigma (Denmark). The cross-linked agent, ECH, was supplied by Merck. The accelerator agent *N,N,N′,N′*-tetramethyl ethylene diamine (TEMED) was supplied by Merck. Sodium hydroxide was used in the preparation of alkaline medium for the cross-linking reactions and it was supplied by Merck. For adsorption studies Mu (5,5´-Nitrilodibarbituric acid mono ammonium salt) was also obtained from Sigma.

2.2. Synthesis of the DEAE-D–ECH hydrogel

Cross-linked DEAE-D–ECH hydrogel was synthesized as following [27]. Different formulations of DEAE-D–ECH hydrogel were prepared by mixing cross-linker ECH (0.5–3%) with different DEAE-D–ECH (90–96%) amounts in the presence of NaOH and 0.01 mL of accelerator, TEMED. After the solution was homogeneously mixed, initiator of 1 mL (0.02 mol/L solution of APS in water) was added. Mixture was stirred magnetically for 2 at 50–55°C. The fresh hydrogel was held in water at room temperature for 7 d in order to remove unreacted monomer, cross-linker, initiator, and the accelerator. The water was replaced with fresh water twice a day. DEAE-D–ECH hydrogel was dried under vacuum at 40°C, until constant weight was reached. The dried hydrogel was characterized with the swelling test. The hydrogel which had the best swelling ratio was used for Mu adsorption experiments.

2.3. Characterization of DEAE-D–ECH hydrogel

FTIR of the DEAE-D–ECH hydrogel and dye adsorbed hydrogel was recorded on a Perkin–Elmer RX-1 Spectrometer in the 4,400–400 cm^{-1}. The surface morphology of DEAE-D–ECH hydrogel and dye adsorbed hydrogel was examined using SEM (JSM 5500, JEOL).

2.4. Measurement of the swelling ratio

For the swelling dynamic studies, the dried samples were placed in dye solution and distilled water at 25°C and removed from solution at regular time intervals. After the surface of the hydrogel was wiped off with moistened filter paper, the weight of the hydrogel was recorded.

The swelling of hydrogel was expressed as swelling ratio by the following equation:

$$S = W_t - W_o/W_o \tag{1}$$

where W_o is the dry weight of hydrogel (initial weight) and W_t is the weight of swollen gel at given time (t).

2.5. Adsorption studies

The adsorption of the dye from aqueous solution was investigated in continuous adsorption equilibrium studies. Equilibrium adsorption experiments were carried out with 50 mL various concentrations of Mu solution with 0.1 g adsorbent at 25˚C, until equilibrium was established. Effect of the initial concentration, contact time, and pH on the adsorption rate and capacity were studied. Dye solutions were prepared by dissolving Mu in deionized water in the concentration range of 5–100 mg/L. After equilibrium, the final concentration C_e was measured. The percentage removal of dye was calculated using the following relationship:

$$\% \text{ removal of dye} = (C_o - C_e/C_o) \times 100 \tag{2}$$

where C_o and C_e are the concentrations of the dye in the initial solution and the aqueous phase, mg/L, after treatment for a certain period of time, respectively.

After adsorption, the dye solution was separated by decantation from the hydrogel. The absorbencies of samples were measured using a UV–Vis spectrophotometer (Hitachi U-1900) at wavelength 520 nm, which is found to be the maximum absorbency for Mu. Then, the concentrations of the samples were determined using linear regression equation $y = 0.0132x$ obtained by plotting a calibration curve for dye over a range of concentrations.

The amount of adsorbed dye per gram of the hydrogel was determined after 24 h. The amount of dye adsorbed onto samples at equilibrium, per unit mass of the DEAE-D–ECH hydrogel was evaluated using the following equation:

$$q_e = C_o - C_e/w \tag{3}$$

where q_e is the amount of dye adsorbed onto unit dry mass of the DEAE-D–ECH hydrogel mg/g, V is the volume of the aqueous phase (L), and w is the amount of dry DEAE-D–ECH hydrogel used (g).

3. Results and discussion

3.1. Characterization of DEAE-D–ECH hydrogel

3.1.1. FTIR study of the hydrogel—before and after the adsorption

The characterization of hydrogel was obtained using FTIR analysis to study the interaction between the dye molecules and the DEAE-D–ECH hydrogel. Fig. 1 shows FTIR spectra of DEAE-D–ECH hydrogel, before and after the adsorption of the dye. The FTIR spectra of the hydrogel show the peak at 1,626 cm^{-1}, which is a characteristic peak of the N–H bonding; after the adsorption of the dye, this band has shifted to 1,666 cm^{-1}. The FTIR spectra of DEAE-D hydrogel after the adsorption of Mu dye shows a peak at 3,200 cm^{-1}, which is originated due to the formation of hydrogen bond between hydrogel and the dye. The presence of band at 3,308 cm^{-1} is due to some quantity of moisture in the hydrogel. It can be seen from the spectra that there is a characteristic peak of the C=O stretching at around 1,727 cm^{-1} due to the presence of carboxyl groups in Mu after adsorption.

3.1.2. Morphology observations

Fig. 2 shows SEM images of DEAE-D–ECH hydrogel formulated at the optimum condition (3% ECH) before and after the adsorption process of the dye, respectively. As seen in these figures, gel is porous, cross-linked, and a matrix, which is shaped fiber. Pores are mostly smooth and shaped ellipse rod per unit area [27]. In the case of dye adsorbed DEAE-D–ECH hydrogel, surface color was changed which may be due to the adsorption of Mu dye molecules on the surface of hydrogel. It was observed that the interstitial spaces of hydrogel were saturated after the application of the adsorbent to the Mu solution.

3.2. Swelling behavior of DEAE-D–ECH hydrogel in water and Mu solution

Water uptake of initially dry hydrogels was followed gravimetrically. Upon swelling, the hydrogel was strong enough to retain its shape. Some researchers have reported that the swelling properties of hydrogels have some relation with their dye adsorption properties [28]. Generally, the equilibrium swelling ratio of a hydrogel is based on structure of dye molecules and the construction of hydrogel. The dynamic swelling curves of DEAE-D–ECH hydrogel in water and Mu solution are given in Fig. 3. As it can be seen from this figure, swelling capabilities of DEAE-D–ECH hydrogel have increased by time and reached constant swelling (equilibrium swelling) after a certain period of time. The percentage of equilibrium swelling of the hydrogels is lower (1,361%) in Mu solution than (1,453%) in water. This lessening is owed to the adsorption of Mu molecules in the gel system with exclusion of water molecules at the expense of the adsorbed molecules, and to the increase in the ionic forces of the equilibrium swelling value of DEAE-D–ECH hydrogel. It is very sensitive to the ionic strength of the swelling medium [29,30].

The dyes contain the unpaired electrons in N and O. These atoms behave like a hydrophilic group and generate hydrogen bonds with water. The DEAE-D–ECH hydrogel has many cationic groups that allow the

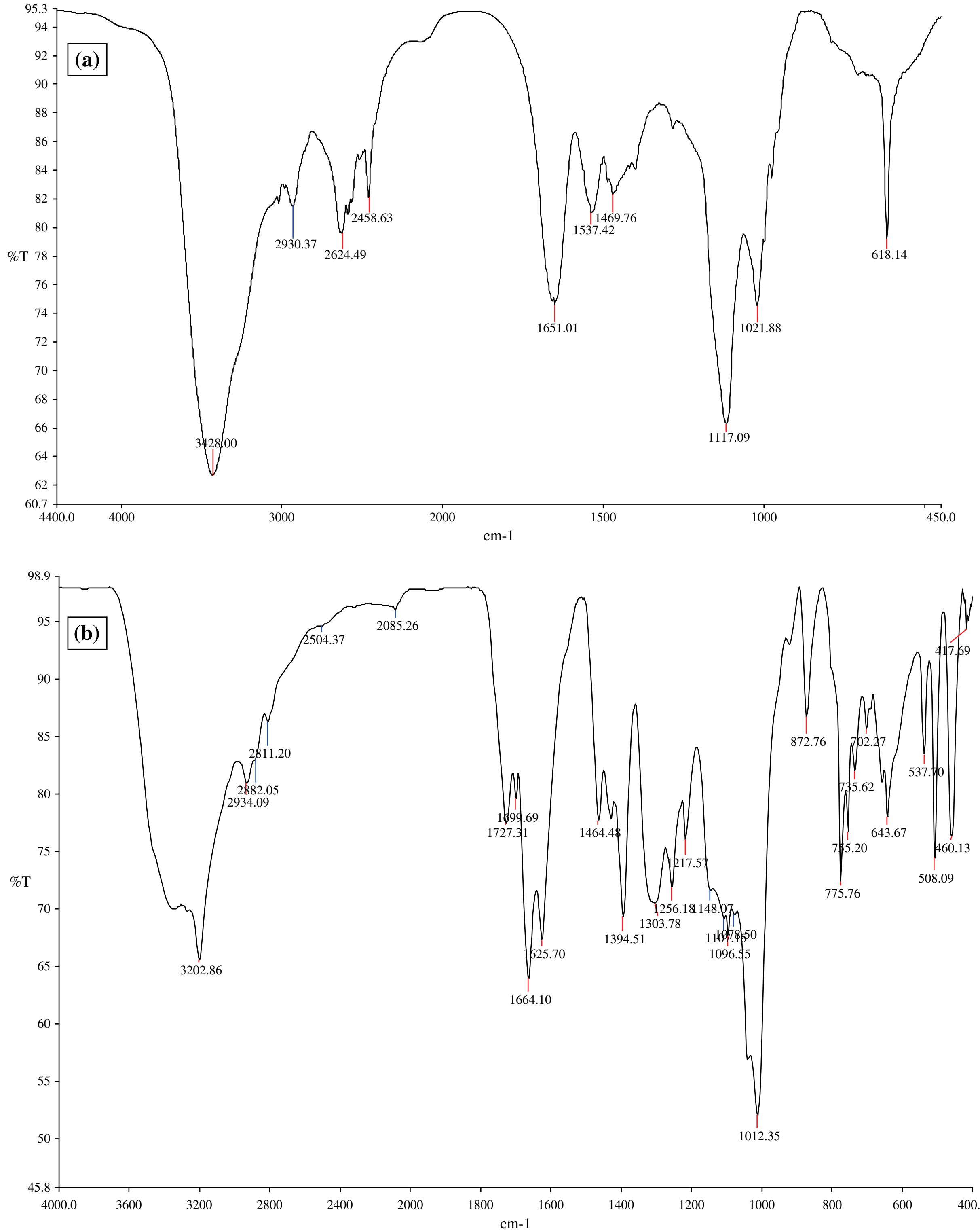


Fig. 1. The FTIR spectra (a) DEAE-D–ECH hydrogel and (b) DEAE-D–ECH hydrogel adsorbed Mu.

increasing interaction between the anionic groups of the anionic dyes and cationic groups of the hydrogel. The mechanism of dye adsorption by the hydrogel is mainly due to the ion exchangeability and the physical interactions, such as dipole–dipole interactions and hydrogen bond formation, between the dye molecules

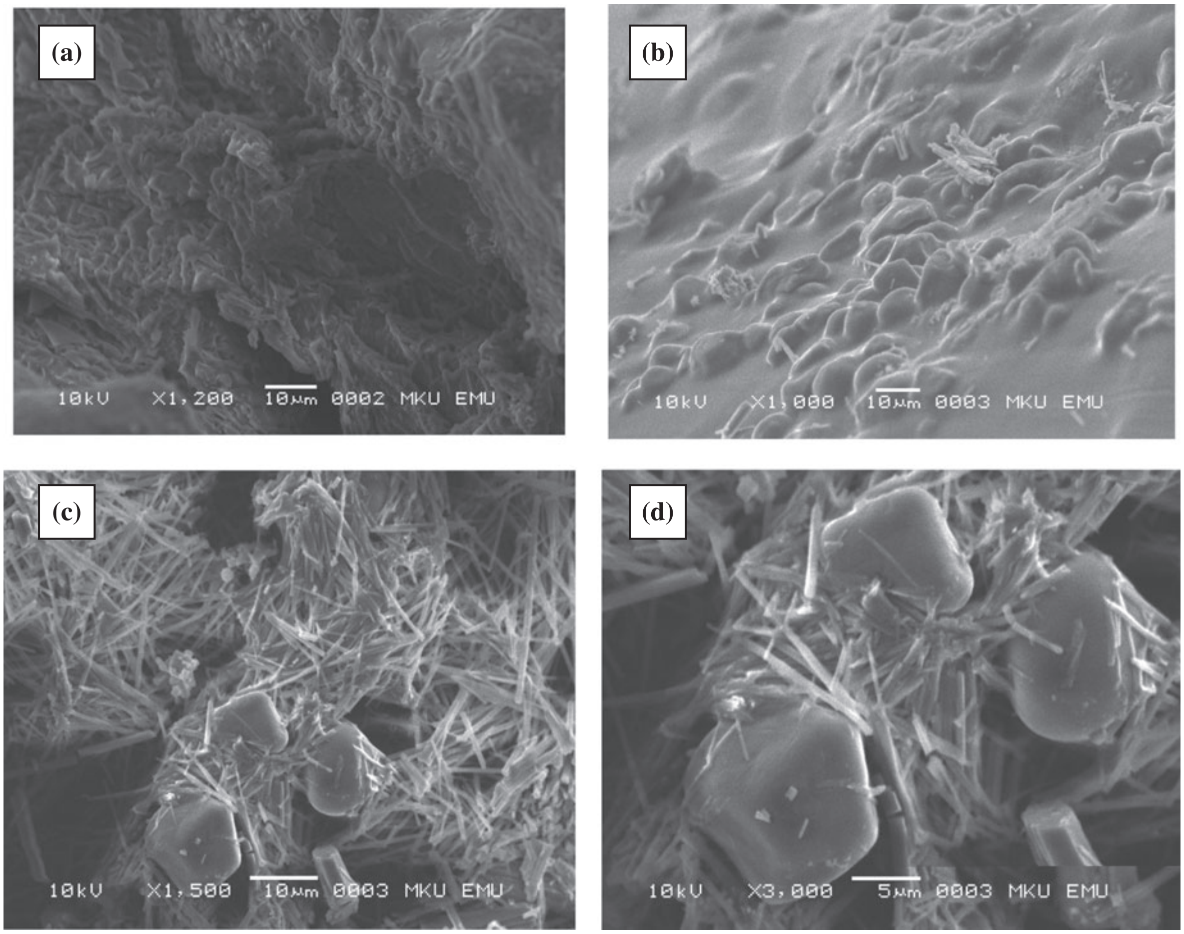


Fig. 2. SEM image of DEAE-D–ECH (a) before and (b)–(d) after the adsorption of Mu dye.

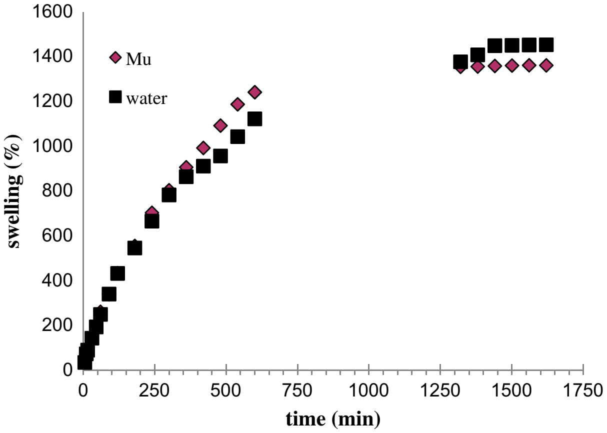


Fig. 3. Kinetic swelling curves of DEAE-D–ECH hydrogel in water and Mu solution (50 mg/L, pH 4, and at 25˚C).

and hydrogel. A typical schematic representation indicating the possible interaction between the cationic dye molecules and DEAE-D–ECH is shown in Fig. 4.

3.3. Adsorption of Mu on DEAE-D–ECH hydrogel

3.3.1. Effect of initial concentration

Fig. 5 shows the effect of initial dye concentration on the equilibrium adsorption of the cross-linked DEAE-D at 25˚C with Mu dye. An increase in initial dye concentration leads to an increase in the adsorption capacity of dye on DEAE-D. This indicates that the initial dye concentration plays an important role in the adsorption capacities of Mu on DEAE-D–ECH hydrogel.

3.3.2. Effect of adsorbent dosage

Adsorbent dosage is one of the important parameters for the adsorption process. The effect of the amount of cross-linked DEAE-D–ECH on the adsorption performance is presented in Fig. 6. The effect of adsorbent dosage on the Mu removal was investigated using different dosages of DEAE-D–ECH ranging from

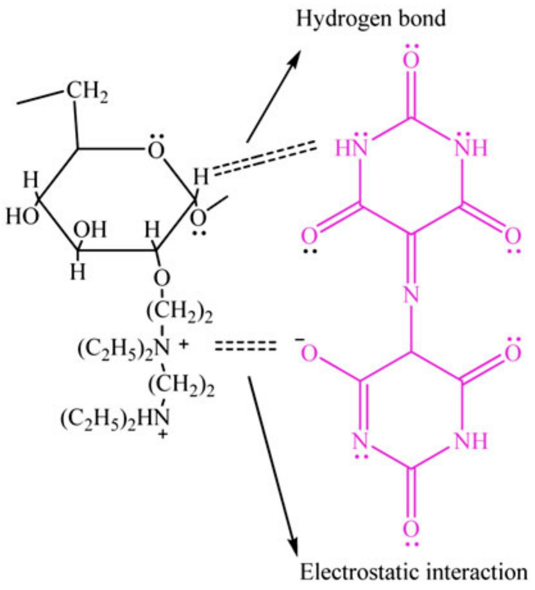


Fig. 4. A possible mechanism of Mu dye adsorption by DEAE-D–ECH hydrogel.

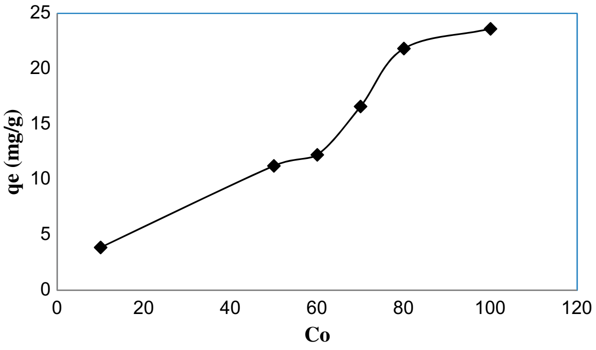


Fig. 5. q_e (mg/g)–C_o graph.

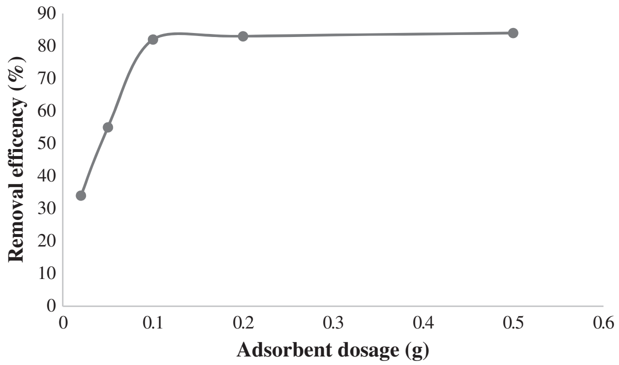


Fig. 6. Effect of adsorbent dosage on the adsorption of Mu from aqueous solutions.

0.02 to 0.5 g in 50 mg/L Mu solutions for 24 h. It was found that, the removal efficiency of Mu by DEAE-D–ECH hydrogel increased as the adsorbent dosage increased from 0.02 to 0.1, the reached about fixed value. As it was expected, adsorption capacities decreased with increase in adsorbent mass due to the reduction in both effective surface area and adsorbate–adsorbent ratio [31,32]. 0.1 g of DEAE-D–ECH was selected as the optimum amount of adsorbent.

3.3.3. Effect of pH on the adsorption behavior

Initial pH of the solution is an important parameter, which affects the adsorption process. It affects not only the surface charge of the adsorbent, but also the ionization degree of the adsorbent. The effect of solution pH depends on the ions present in the reaction mixture and electrostatic interactions at the adsorption surface. To determine the effect of different pH on Mu dye removal, experiments were carried out by adjusting the pH value to 2, 7, and 10 using acid–base buffer solutions. The effect of pH on the dye adsorption was investigated at an initial concentration of 50 mg/L in presence of 0.1 g of hydrogel, and illustrated in Fig. 7.

The maximum dye removal was observed (above 87%) at pH 4. The reason for reaching maximum adsorption, of hydrogel, at pH 4 is that protonization of amine groups of DEAE-D is completed at this pH value [33]. The electrostatic attraction between the positively charged N^+ ions and negatively charged dye results in the formation of ionic complex, which increases the dye removal. This increase may result due to the bond of NH_2 groups with protons to form complexes, and thereby leading the surface of the sample to be positively charged [34,35].

$$R\text{–}NH_2 + H^+ \leftrightarrow R\text{–}NH_3^+$$

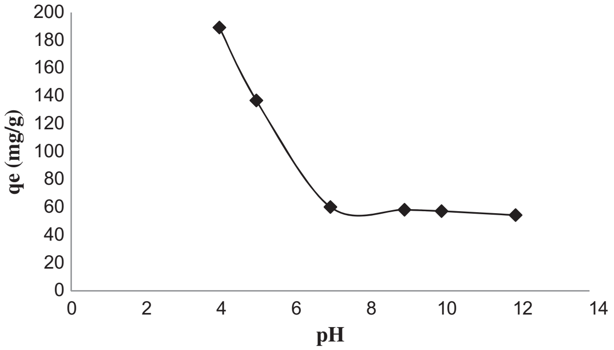


Fig. 7. Effect of pH on the adsorption of Mu by DEAE-D–ECH hydrogel. (50 mg/L, at 25°C).

3.3.4. Effect of contact time

The effect of contact time on the percentage of Mu dye with 50 mg/L initial dye concentration was studied pH 4 at 25°C. The percentage removal of the Mu by DEAE-D–ECH was rapid in the beginning, but it increasingly decreased with time until it reached equilibrium. The equilibrium time was approximately 24 h. As seen in Fig. 8, at equilibrium DEAE-D–ECH hydrogel had adsorbed 82% of Mu dye from the solution.

3.3.5. Adsorption isotherm models

The non-linear forms of Langmuir and Freundlich isotherm models were used to analyze the equilibrium isotherm data and these models were evaluated by the non-linear coefficients of determination (R^2). The expression of the Langmuir model is given as:

$$q_e = (q_m K_L C_e)/(1 + K_L C_e) \tag{4}$$

where C_e is the equilibrium concentration of Mu mg/L in the solution; q_e is the equilibrium Mu concentration on the adsorbent; and q_m (mg/g) and K_L (L/mg) are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively.

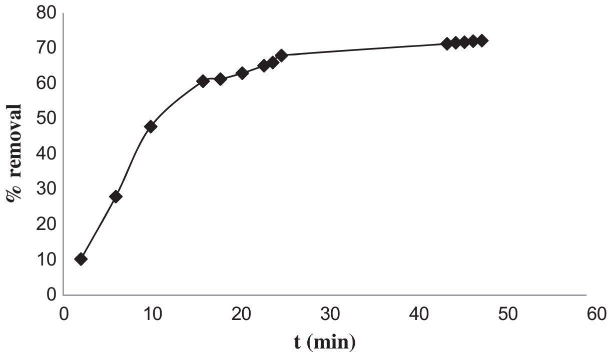


Fig. 8. Effect of contact time on the adsorption of Mu by DEAE-D–ECH hydrogel. (50 mg/L, pH 4 at 25°C).

Freundlich isotherm is represented by the following equation;

$$q_e = K_f C_e^{1/n} \tag{5}$$

where n is the heterogeneity factor and K_f is the Freundlich constant L/g. The theoretical parameters of adsorption isotherms along with regression coefficients R^2 are listed in Table 1 that shows dependent equilibrium data on Langmuir and Freundlich models for Mu adsorption. The correlation coefficients R^2 of Langmuir and Freundlich models were 0.996 and 0.987, respectively; so, the Langmuir adsorption law is applicable to the adsorption of Mu onto DEAE-D–ECH. The Langmuir isotherm is based on the assumption that a point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule [36].

In addition, the Langmuir parameter R_L obtained from the Langmuir adsorption isotherm model is used to predict the favorability of the adsorption process. The R_L was calculated from the following equation using the Langmuir K_L parameter:

$$R_L = 1/(1 + K_L C_o) \tag{6}$$

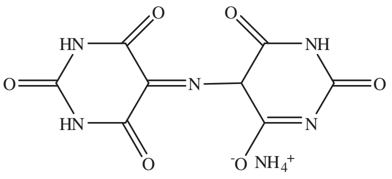
where C_o, mg/L is the initial concentration.

Isotherm is considered to be unfavorable ($R_L > 1$), linear ($R_L = 1$), and favorable ($1 > R_L > 0$) or irreversible ($R_L = 0$) depending on the value of R_L. The R_L value is 0.0083 indicating that Mu adsorption on DEAE-D–ECH hydrogel is a favorable and practical process.

3.3.6. Kinetics of Mu adsorption

An ideal adsorbent for wastewater pollution control must not only have a large adsorbent capacity, but also a fast adsorption rate [25]. To analyze the adsorption rate of Mu onto cross-linked DEAE-D–EC the last one is collected by three simple kinetic models: Lagergren-first-order and pseudo-second-order

Table 1
Chemical structure and some physical properties of Mu dye

Name	Chemical formula	Molecular mass	Color index No.	λ_{max} (nm)
Murexide (Mu)		284.19	56085	520

kinetic models and the intraparticle mass transfer diffusion model [37]. The models were evaluated based on the experimental data.

The Lagergren-first-order model is expressed as,

$$\log\,(q_e - q) = log\ q_e - k_1/2.303) \times t \tag{7}$$

where q_e and q are the amounts of dye adsorbed on adsorbent at equilibrium and at time t, respectively (mg/g), and k_1 is the rate constant of first-order adsorption min^{-1}. The slopes and intercepts of plots of *log* $(q_e - q)$ and t were used to determine the first-order rate constant k_1.

The pseudo-second-order kinetic model is expressed as,

$$t/q_t = 1/k_2 q_e^2 + t/q_e \tag{8}$$

where k_2 (g/mg min) is the rate constant of second-order adsorption. The slopes and intercepts of plots of t/q_t and t were used to calculate the second-order rate constant k_2 vs. q_e.

The intraparticle mass transfer diffusion model is expressed as;

$$q_t = K_{id} t^{1/2} + c \tag{9}$$

where c is the intercept (mg $\text{min}^{1/2}$/g) and K_{id} is the intraparticle diffusion rate constant, which can be evaluated from the slope of the linear plot of q_t vs. $t^{1/2}$. Kinetic parameters of Mu adsorption on DEAE-D–ECH hydrogel are given in Table 2.

Table 2
Langmuir and Freundlich isotherm constants for Mu (pH 4 at 25℃)

Langmuir				Freundlich		
K_L	q_m	R_L	R^2	K_f	n	R_2
557.24	206.50	0.0000358	0.99	0.43898	1.019	0.97

Note: Initial Mu concentration was 50 mg/L.

Table 3
Lagergren-first-order, pseudo-second-order, and intraparticle mass transfer diffusion models' kinetic parameters for removal of Mu by DEAE-D–ECH hydrogel

Lagergren-first-order kinetic model			Pseudo-second-order kinetic model			Intraparticle mass transfer diffusion model		
q_e	k_1	R^2	q_e	k_2	R^2	k_{id}	c	R^2
0.623	0.223	0.94	0.883	0.264	0.99	0.025	0.665	0.98

3.3.7. Thermodynamic parameters

The thermodynamic parameters, such as Gibbs free energy change ΔG°, standard enthalpy change ΔH°, and standard entropy change ΔS°, were also studied in order to have a better understanding of the effect of temperature on the adsorption. These parameters can be calculated using the thermodynamic equilibrium coefficient obtained at different temperatures. Adsorption experiments were studied at 288, 298, 308, and 318 K in order to investigate the effect of temperature, with 50 mg/L of initial Mu concentration and 0.1 g of DEAD-D–ECH hydrogel.

$$K_c = q_e/C_e \tag{10}$$

$$\text{Gibbs } \Delta G^\circ = -RT \ln K_c \tag{11}$$

$$\text{van't Hoff In } \mathrm{K}_c = (\Delta \mathrm{H/RT}) + \Delta \mathrm{S}^\circ/\mathrm{R} \tag{12}$$

where ΔG° (kJ/mol), ΔH° (kJ/mol), and ΔS° (kJ/mol K), R is the universal gas constant (8,314 J/mol K) and T is the solution temperature in Kelvin (K); and K_c is the equilibrium constant.

Table 4
Thermodynamic parameters for the adsorption of Mu onto DEAE-D–ECH hydrogel

	Thermodynamic parameters				
T/K	K_c (L/mg)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol)	R^2
323	5.897	−15,836.2	1,17,084.201	410.01	0.99
313	4.282	−11,143.7			
308	3.413	−8,741.79			
303	2.677	−6,745.48			
298	2.040	−5,056.39			
293	1.466	−3,571.96			

ΔH° and ΔS° of the adsorption are calculated from the slope and intercept of the van't Hoff plots of ln Kc vs. $1/T$. The complete adsorption and thermochemical data are given in Table 3.

4. Conclusions

The potential for the use of DEAE-D–ECH hydrogel for the removal of reactive dye Mu was investigated in this study. Adsorption of the dye was studied by the batch technique and it was observed using of DEAE-D–ECH hydrogel. The effect of process parameters, such as contact time, initial concentration of the dye solution, adsorption temperature, and pH value of the dye solution for the removal of Mu from aqueous solution, was also studied. The results showed that the adsorption capacity for Mu increased with increase in contact time, initial dye concentration, but decreased with pH value. The kinetic adsorption was better described by the pseudo-second-order equation. Equilibrium data were fitted to Langmuir and Freundlich isotherms and the equilibrium data were best described by the Langmuir isotherm model. The positive ΔH° value indicated the endothermic nature of the adsorption interaction, whereas the positive ΔS° value showed the increased randomness at the solid–solution interface during the adsorption process. The negative value of ΔG° indicated the feasibility and the spontaneous nature of the adsorption of Mu onto DEAE-D–ECH hydrogel Table 4.

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