Eriochrme black-T removal from aqueous environment by surfactant modified clay: equilibrium, kinetic, isotherm and thermodynamic studies

Article *in* Toxin Reviews · March 2018

DOI: 10.1080/15569543.2018.1455214

Yusef Omidi

Ahvaz Jondishapour University of Medical Sciences

45 PUBLICATIONS **243** CITATIONS

SEE PROFILE

Heshmatollah Nourmoradi

Ilam University of Medical Sciences

102 PUBLICATIONS **359** CITATIONS

SEE PROFILE

Shirin Esmaeili

6 PUBLICATIONS **2** CITATIONS

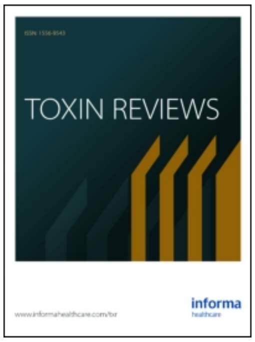
SEE PROFILE

Mohammad Javad Mohammadi

Allameh Tabatabai University

93 PUBLICATIONS **503** CITATIONS

SEE PROFILE



Taylor & Francis
Taylor & Francis Group

Toxin Reviews

ISSN: 1556-9543 (Print) 1556-9551 (Online) Journal homepage: http://www.tandfonline.com/loi/itxr20

Eriochrme black-T removal from aqueous environment by surfactant modified clay: equilibrium, kinetic, isotherm, and thermodynamic studies

Ghader Zeydouni, Mahsa Kianizadeh, Yusef Omidi Khaniabadi, Heshmatollah Nourmoradi, Shirin Esmaeili, Mohammad Javad Mohammadi & Rajab Rashidi

To cite this article: Ghader Zeydouni, Mahsa Kianizadeh, Yusef Omidi Khaniabadi, Heshmatollah Nourmoradi, Shirin Esmaeili, Mohammad Javad Mohammadi & Rajab Rashidi (2018): Eriochrme black-T removal from aqueous environment by surfactant modified clay: equilibrium, kinetic, isotherm, and thermodynamic studies, Toxin Reviews

To link to this article: https://doi.org/10.1080/15569543.2018.1455214

TOXIN REVIEWS, 2018
https://doi.org/10.1080/15569543.2018.1455214

Taylor & Francis
Taylor & Francis Group

RESEARCH ARTICLE

Eriochrme black-T removal from aqueous environment by surfactant modified clay: equilibrium, kinetic, isotherm, and thermodynamic studies

Ghader Zeydouni[a], Mahsa Kianizadeh[b], Yusef Omidi Khaniabadi[c], Heshmatollah Nourmoradi[d,e], Shirin Esmaeili[f], Mohammad Javad Mohammadi[g] and Rajab Rashidi[h]

[a]Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Science, Tehran, Iran; [b]Department of Environmental Health Engineering, Shahrekord University of Medical Sciences, Shahrekord, Iran; [c]Department of Environmental Health Engineering, Health Care System of Karoon, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran; [d]Biotechnology and Medical Plants Research Center, Ilam University of Medical Sciences, Ilam, Iran; [e]Department of Environmental Health Engineering, School of Health, Ilam University of Medical Sciences, Ilam, Iran; [f]Department of Environmental Health Engineering, School of Public Health, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran; [g]Asadabad School of Medical Sciences, Asadabad, Iran; [h]Department of Occupational Health Engineering, Nutrition Health Research Center, School of Health and Nutrition, Lorestan University of Medical Sciences, Khorramabad, Iran

ABSTRACT

In this study, the removal of Eriochrome black T (EBT) from aqueous solutions was evaluated by cationic surfactant of hexadecyl trimethyl ammonium bromide (HDTMA)-modified montmorillonite clay (MC). The effects of contact time, pH, adsorbent dosage, EBT concentration, solution ion strength, and temperature were investigated on the EBT removal. HDTMA-MC was also examined by Fourier transformed infrared (FTIR) spectroscopy and X-ray diffractometer (XRD). The results illustrated that the experimental data were well followed by the pseudo-second-order kinetic and Freundlich isotherm models. The results also showed HDTMA-MC can be used as an effective adsorbent for the removal of EBT from aqueous solution.

ARTICLE HISTORY
Received 22 December 2017
Revised 15 March 2018
Accepted 18 March 2018

KEYWORDS
Adsorption; cationic surfactant; montmorillonite; eriochrome black T

1. Introduction

Water pollution due to discharging of industrial effluents into the environment is considered as an important environmental problem in the current century especially in developing countries (Lin *et al*. 2013, Basiri *et al*. 2015, Ahmadi *et al*. 2016, Omidi-Khaniabadi *et al*. 2016, Biglari *et al*. 2018). Disposal of dye containing wastewaters resulted from industrial activities into the water bodies due to their toxic properties can cause adverse health effects on the aquatic life as well as human. Most of the dyes are carcinogenic, mutagenic, and teratogenic, so have adverse effects on the human health. Because of these properties, the removal of dyes from industrials wastewater before their discharge into the rivers is necessary (Khaniabadi *et al*. 2016, Mohammadi *et al*. 2017). Eriochrome black T (EBT) as a model of azo dyes is allocated more than 50% of dye manufacture in the world. This dye usually used for applications such as dyeing silk, nylon, and wool (Barka *et al*. 2011, Arfi *et al*. 2017a, 2017b, Zubair *et al*. 2017). EBT is a toxic compound that its degradation can lead to making a carcinogenic phenolic matter. Wastewaters containing azo dyes are difficult to biological treatment because they contain azo groups with aromatic rings and sulfonate groups (Mittal and Gupta 2010, Dave *et al*. 2011). These groups are resistant to degradation in aerobic digestion and oxidation agent conditions. Azo dyes are stable to light, heat, chemical, and microbial degradation, even at low concentration (Moeinpour *et al*. 2014, Arfi *et al*. 2017a, 2017b). A number of methods include coagulation, ozonation, chemical oxidation, electrochemical methods, ion exchange, membrane processes, and adsorption have been studied to treat dying effluents. In the recent years, adsorption process has been widely applied to the treatment of industrials colored wastewaters (Khaniabadi *et al*. 2017). Although activated carbon due to having high adsorption capacity is the most frequently used for this purpose, it is expensive and hard to recover. Recently, a number of cheap and available adsorbents including eucalyptus bark (Dave *et al*. 2011), Moroccan clay (Elmoubarki *et al*. 2015), sawdust (Khattri and Singh 2009), red mud (Wang *et al*. 2005), Ca-bentonite

CONTACT Rajab Rashidi rajab_rashidi@yahoo.com, rashidi.r@lums.ac.ir Department of Occupational Health Engineering, Nutrition Health Research Center, School of Health and Nutrition, Lorestan University of Medical Sciences, Khorramabad, Iran

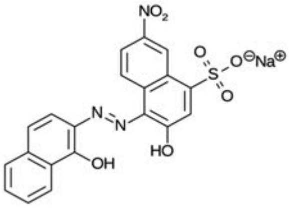
(Lian *et al*. 2009), chitosan/bentonite composite (Liu *et al*. 2015), rice husks (Lin *et al*. 2013), etc., have been advanced to the removal of dyes from aqueous solutions. Montmorillonite is a natural component that commonly used as an adsorbent to remove different organics and inorganics pollutants (Alex *et al*. 2017, Cheng *et al*. 2017). This clay has a number of properties such as low-cost, high sorption capacity, high surface area, eco-friendly, and non-toxicity which caused considered as a suitable adsorbent for dyes adsorption from aqueous media (Mohammadi *et al*. 2017). Due to its hydrophilic nature, there is needed the modification of the clay surface by organophilic substances such as surfactants (Khaniabadi *et al*. 2017). Also, it has been proved that the intercalation of cationic surfactants modifies the surface properties of montmorillonite from hydrophilic to hydrophobic through cation exchange (Omidi-Khaniabadi *et al*. 2016). In this study, the surface of montmorillonite clay was modified by cationic surfactant of hexadecyl trimethyl ammonium bromide and then used as an adsorbent for the removal of Eriochrome black T from polluted water. The influences of contact time, pH, adsorbent dosage, initial dye concentration, ionic strength, and temperature were explored on EBT removal from aqueous solutions.

2. Materials and methods

2.1. Materials

The montmorillonite clay (MC) and also the hexadecyl trimethyl ammonium bromide (HDTMA) were purchased from Laviosa Co, Livorno, Italy and Aldrich Co, St. Louis, MO, respectively. All the other chemicals including EBT dye, H_2SO_4, NaOH, and $CaCl_2$ used in this study were of analytical grade and supplied from Merck Co, Darmstadt, Germany. Table 1 shows general properties and the chemical structure of EBT dye. The pH value of the solution was adjusted via adding of 0.1 N H_2SO_4 or NaOH solutions by a digital pH-meter. The EBT stock solution (100 mg/L) was prepared by dissolving 100 mg of EBT in 1 L distilled water and subsequently the required concentrations were achieved using dilution of the stock solution.

Table 1. The general characteristics of the EBT dye.

Characteristic	EBT	Chemical structure
General name	Eriochrome Black T	
Chemical formula	$C_{20}H_{12}N_3O_7SNa$	
Molecular weight (g/mol)	461.38	
Dye type	Azo dye	
Color type	Brownish black	
Appearance	Powder	
Nature	Anionic	
λ_{max} (nm)	560	

2.2. Purification and modification of montmorillonite

To purify of MC, 30 g of the clay was placed in 1 L of deionized water. The solution was mechanically stirred at 250 rpm for 24 h at room temperature (25 °C ± 2 °C). Then the obtained suspension was centrifuged at $1790 \times g$ for 20 min to eliminate impurities and the supernatant was collected, dried at 105 °C and then sieved to a particle size less than 125 μm (Nourmoradi *et al*. 2012).

In order to modify the clay by HDTMA in the amounts of 0.2–2 Mmol (20–200%) of the MC cationic exchange capacity (CEC), 5 g of highly purified MC was separately introduced in 100 ml of deionized water (1:20) and mixed with 0.393, 0.984, 1.37, 2.36, 2.95, and 3.93 g of the cationic surfactant to produce HDTMA-modified MC at surfactant loadings of 20, 50, 70, 120, 150, and 200% of the MC CEC, respectively. The suspensions were agitated on a stirrer at 250 rpm for 24 h at room temperature. The HDTMA-modified MC was centrifuged at $1790 \times g$ for 20 min, washed several times with deionized water, then dried at 60 °C and finally passed through an ASTM (American Standard Test Sieve Series) sieve of 125 μm (mesh no. 120).

2.3. Characterization and analysis

The specific surface area and the morphology of the raw-MC and HDTMA-MC were characterized by Sears's method and by SEM (Jeol Model Jsm-T330, Jeol, Tokyo, Japan), respectively (Nourmoradi *et al*. 2012). FTIR spectral study of the raw and HDTMA-modified MC was analyzed by Diffuse Reflectance FTIR spectroscopy (DRIFTS-FTIR) at a resolution of 1 cm^{-1} in the region of 400–4000 cm^{-1} (JASCO, FT/IR-6300, Kyoto, Japan). The characterization of the MC was also determined by X-ray diffractometry (Bruker, D8 Advance, Bremen, Germany) using Ni filtered Cu K*a* radiation (1.5406 A°). The concentrations of EBT in the solution were measured by a UV–vis spectrophotometer (PG Instrument Limited Model, PG Instrument Limited, Norwood, MA) and associated with the maximum absorption peak in the visible wavelength spectrum of 560 nm.

2.4. Adsorption experiments

In a batch approach, the effect of surfactant loading rates (20–200% CEC of the MC), contact time (0–120 min), pH (3–11), adsorbent dosage (1–10 g/L), adsorbate concentrations (20–200 mg/L), ion strength of solution (20–100 mol/l Ca^{2+} ions), and temperature (15–45 °C) on the removal of EBT were examined. All the uptake experiments were conducted using 100 mL of dye solution at room temperature (25 °C ± 2 °C) in 250 mL conical flask containing 1 g/L of adsorbent on a mechanical stirrer (250 rpm). After attaining the equilibrium time, the suspensions were centrifuged at $1370 \times g$ for 20 min, then the supernatant was determined through a UV–vis spectrophotometry. Batch adsorption experiments were conducted in duplicate and calculated averages were presented. The adsorption capacity (mg/g) of the modified MC for EBT removal was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)\,V}{m} \tag{1}$$

where q_e (mg/g) is the uptake capacity of the dye, C_0 is the initial dye concentration, and C_e (mg/L) is the equilibrium dye concentration. Also, V (L) is the solution volume and m (g) is the adsorbent mass (Elmoubarki *et al.* 2015).

3. Results and discussion

3.1. Characterization

3.1.1. Characterization of the adsorbent

The physicochemical characteristics of the MC are exhibited in Table 2. As can be seen, SiO_2 and Al_2O_3 were the major constituents of the adsorbent together with other oxides present in lower quantities. Therefore, it was expected the major oxides in the adsorbent was responsible for the dye uptake from the solutions. On the basis of Sear's method, the CEC of the MC was 108 meq/100 g (Nourmoradi *et al.* 2012).

Table 2. Composition of the MC used in the present study (Nourmoradi *et al.* 2012).

Compound	(%) Amount
SiO_2	60.00
Al_2O_3	20.03
Fe_2O_3	2.31
Na_2O	3.02
P_2O_5	0.05
MgO	4.02
K_2O	0.13
CaO	1.46
TiO_2	0.24
MnO	0.03
H_2O	8.71
CEC (meq/100 g)	108
Limit of ignition (%)	7.03

3.1.2. Surface area measurement

The results of surface area measurement showed that the adsorbent modification of the raw MC by HDTMA led to a reduction of the MC surface area from 32.6 m^2/g for the raw MC to 27.8 m^2/g for HDTMA-modified MC. This reduction in the surface area of the modified-MC can be linked to the blocking of some of the internal layers of the HDTMA-modified MC by the surfactant. The modification of MC led to a smaller surface area, but its adsorption capacity increased due to the shift of the MC surface from hydrophilic to hydrophobic.

3.1.3. SEM images

The SEM images of the raw and modified-MC are illustrated in Figure 1. As can be seen, the raw MC (left) has an irregular shape with an uneven surface structure. In contrast, the HDTMA-modified MC (right) has a homogenous and smoother surface and the surfactant particles are seen upon it. Indeed, the organic surfactant-modified clay shows significant changes in the morphology. There are several small and aggregated particles and the sheets become relatively flat layers compared with the morphology of the Na–montmorillonite. In modified clay, the cationic surfactant easily intercalated into the clay interlayer space by cation exchange. In this case, intercalation of the cationic surfactants not only changes the surface properties of clays from hydrophilic to hydrophobic but also increases the basal spacing of the clay interlayers. There was found that modified montmorillonite by HDTMA expanded the average pore size and interlamellar space due to the insert of HDTMA cations into the aluminosilicate sheets of the clay. Other studies showed that the adsorption of amines ions on montmorillonite surface involves three types of reactions including cation-exchange reaction, ion pair adsorption, and interactions of tail–tail. So, the adsorption mechanisms are closely related to the size of quaternary amines (Zhang *et al.* 1993, Krishna *et al.* 2001). Zhang *et al.* (2017) pointed out that the hydrophobic tails interaction between HDTMA surfactants can also bring out positive charge development on the surface of montmorillonite. Their results also showed that larger HDTMA cations may insert into the aluminosilicate sheets and then expand the interlamellar space (Zhang *et al.* 2017).

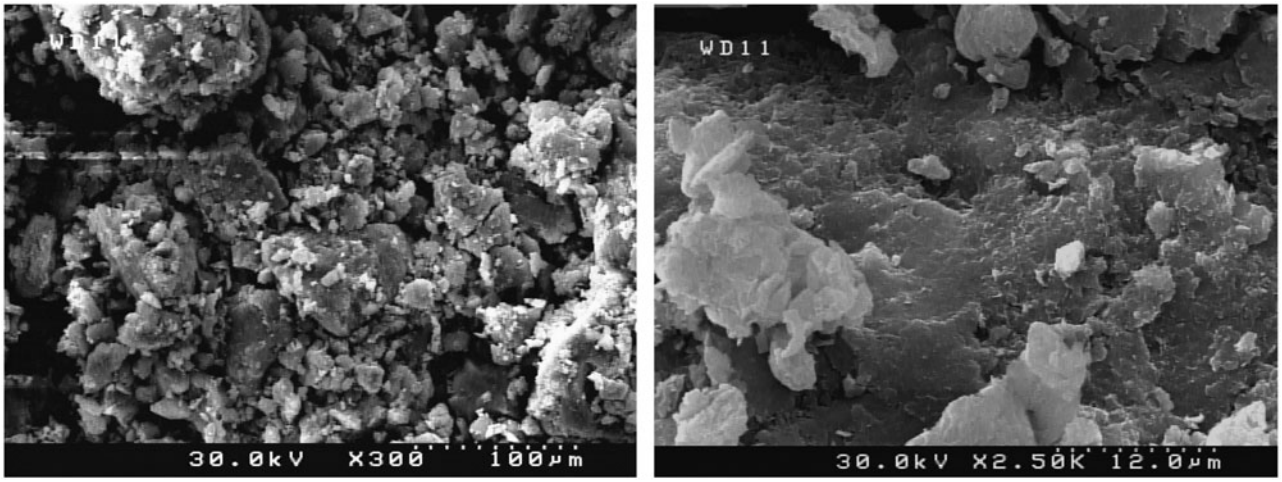


Figure 1. SEM image of raw MC (left) and HDTMA-modified MC (right).

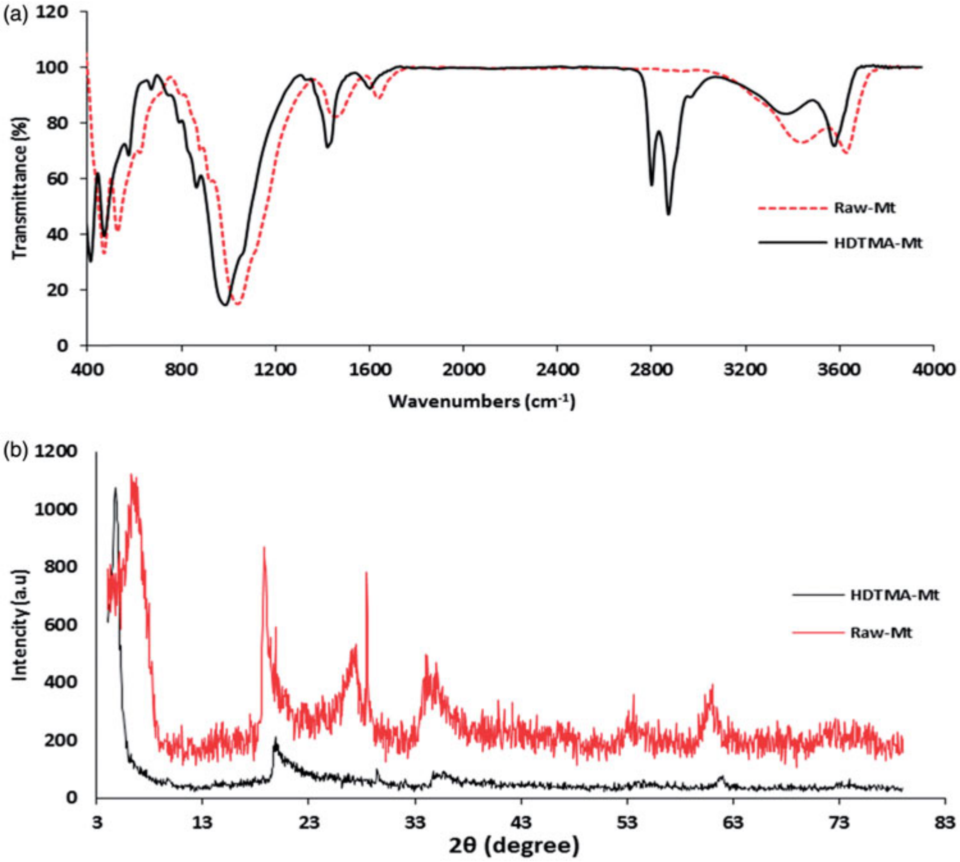


Figure 2. (a) FTIR spectra and (b) XRD patterns of the raw MC and HDTMA-MC.

3.1.4. FTIR analysis

The FTIR spectra of the raw MC and HDTMA-modified MC are depicted in Figure 2(a). The raw MC and the HDTMA-modified MC showed similar peaks in the region of 400–2000 cm^{-1}. FTIR spectra of the raw MC and the HDTMA-modified MC are different in the region of 2800–3000 cm^{-1} (Omidi-Khaniabadi *et al.* 2016). As shown, the characteristic bands at 3627 cm^{-1} and the wide band at 3436 cm^{-1} are related to –OH and H_2O stretching vibrations, respectively (Nourmoradi *et al.* 2012). The IR band at 1635 cm^{-1} is associated to water molecules bound to Al and Mg (Su *et al.* 2011). Also, the decrease in the IR band intensity of 1635 cm^{-1} in the HDTMA-modified MC indicates a reduction of the water content due to the replacement of the hydrated cations with the surfactant. These changes showed that the features of the adsorbent surface were altered from hydrophilic to hydrophobic by the modification with the HDTMA surfactant. The IR bands at 1036 cm^{-1}, 525 cm^{-1}, and 468 cm^{-1} were attributed to the stretching vibration of Si–O, Al–O–Si, and Si–O–Si groups, respectively (Silva *et al.* 2012, Omidi-Khaniabadi *et al.* 2016). The new broad peak found in the region of 2800–3000 cm^{-1} in the modified adsorbent can be assigned to the stretching vibration of the C–H groups. The appearance of this peak can be due to the intercalation of the surfactant into the MC (Nourmoradi *et al.* 2012). This renders MC organophilic which plays an important role in the removal of the above-mentioned pollutants.

3.1.5. XRD analysis

A powerful technique to prove the loading of the surfactants in the galleries of the resulting organoclay is XRD analysis. The XRD patterns of the raw MC and HDTMA-modified MC are illustrated in Figure 2(b). As observed, the modification of the raw MC by the HDTMA surfactant led to structural changes in the MC (Omidi-Khaniabadi *et al.* 2016). The XRD basal spacing in the raw MC was 12.10 Å. The interlayer spacing of the HDTMA-modified MC increased to 18.83 Å which showed that HDTMA molecules were inserted into the internal region of the MC (Nourmoradi *et al.* 2012).

3.2. Effects of the surfactant-loading rate on dye removal

The removal of EBT by HDTMA-modified MC at different loading rates of the surfactant (20–200% of the CEC MC) is displayed in Figure 3. As shown, the adsorption capacity (q_e) of the HDTMA-modified MC incremented up to 70% of the CEC MC. The high surfactant loading may occupy the whole internal layers spaces of the MC and as a result, the diffusion of adsorbate into these layers was reduced. The adsorption capacity of EBT by the HDTMA-modified MC in 70% of the CEC MC was 79.8 mg/g. Therefore, the MC with the surfactant-loading yields of 70% CEC of the adsorbent was considered for the subsequent experiments.

3.3. Effect of contact time

The effect of different contact times (0–120 min) on the adsorption of EBT with MC the surfactant-loading yields of 70% CEC in 100 mL dye solution (100 mg/L) and 1 g/L adsorbent at the initial pH was evaluated and the results are illustrated in Figure 4(a). As seen, a rapidly uptake was observed in the beginning of the process and, therefore, the equilibrium attained in the time of 30 min and, after that, the uptake capacity reached to a fixed state during the remaining contact time up to 120 min. The quick adsorption of EBT onto MC at the initial contact time may be the relation to the accessibility of high numbers of the unfilled sites in the surface of the HDTMA-modified MC and these sites then occupied by the dye as the time went ahead. Barka *et al.* (2011) stated that the equilibrium time for the adsorption of EBT by Scolymus hispanicus was achieved at the time of 45 min in 100 mg/L EBT concentration (Barka *et al.* 2011). Djomgoue *et al.* (2012) also reported that the equilibrium time for the adsorption of EBT via magnetic clay was achieved in 20 min. They also indicated that the sorption capacity of Kob and magnetic clays for EBT was 2.12 mg/g and 1.5 mg/g, respectively (Djomgoue *et al.* 2012).

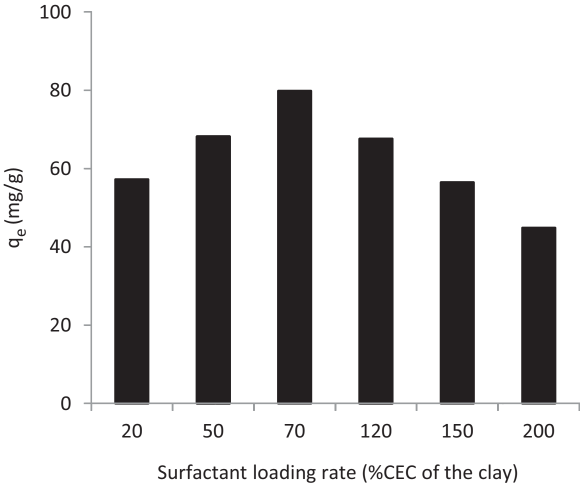


Figure 3. Effect of the surfactant loading rate on the adsorption of EBT by HDTMA-modified MC (EBT = 100 mg/L, contact time = 24 h, HDTMA-modified MC dosage = 1 g/L).

3.4. Effect of solution pH

The influence of solution pH on the adsorption capacity of EBT onto HDTMA-modified MC surface was investigated over the pH ranging 3–11. As it can be seen in Figure 4(b), the adsorption value of the adsorbent was decreased with increase in the initial pH from 3 to 11. The maximum adsorption (91.98 mg/g) has occurred in pH of 3. This result can be because of the change onto the surface charges of the HDTMA-modified MC. The quantity of positive charges to the HDTMA-modified MC was worse improved by the decreasing of initial solution pH, subsequently resulted in the adsorption capacity was increased in

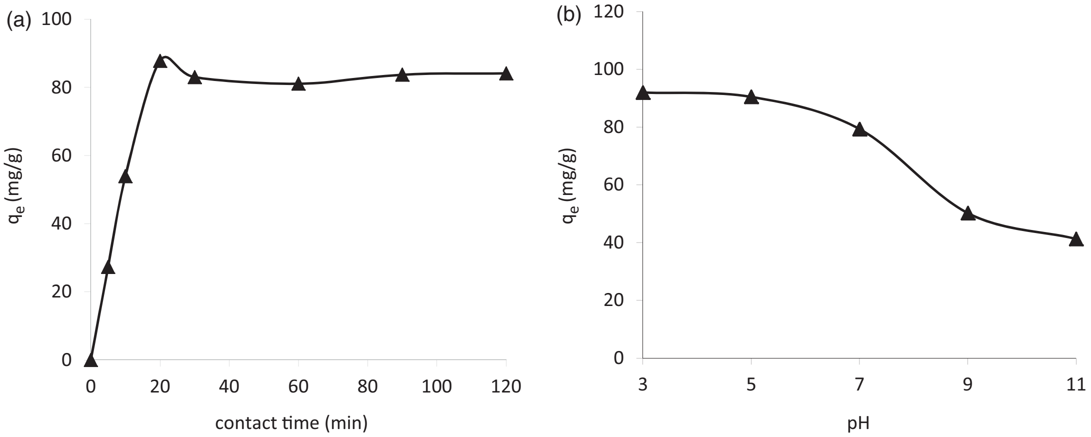


Figure 4. (a) Effect of contact time on EBT adsorption (concentration of EBT = 100 mg/L and adsorbent dosage = 1 g/L) and (b) effect of pH (contact time = 30 min, EBT concentration = 100 mg/L, adsorbent dosage = 1 g/L).

more acidic solution pH. Besides, the electrostatic repulsions between the negatively charged adsorbent and anionic dye of EBT are increased in the basic pH. Therefore, pH of 3 was selected as the optimum pH for the next stages. The similar results were found to be by Barka *et al*. (2011) for the uptake of EBT by Scolymus hispanicus (Barka *et al*. 2011). Djomgoue *et al*. (2012) also showed that the highest removal of EBT by magnetic clay was found to be in acidic pH of 2 (Djomgoue *et al*. 2012).

3.5. Kinetics study

The data of kinetics provide useful information for determining the adsorption process mechanism. In this study, two kinetic models including pseudo-first-order and pseudo-second-order kinetics were applied to analyze the experimental data of EBT adsorption on the HDTMA-modified MC surface.

The pseudo-first-order kinetic assumes the adsorption rate of adsorbent is proportional to the driving force (i.e. the difference between the adsorption capacities in equilibrium and actual state) and the adsorbed amount (Dave *et al*. 2011, Tanzifi *et al*. 2018) can be depicted by the following equation:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{2}$$

where q_e (mg/g) and q_t (mg/g) are the quantities of EBT adsorbed onto the HDTMA-modified MC at the equilibrium and at any time (min), respectively. K_1 (1/min, the rate constant of the pseudo-first-order model) and q_e were gained from the slope and intercept of the liner plot of $\ln\left(q_e - q_t\right)$ against t, respectively (Zubair *et al*. 2017).

Table 3. Parameters of pseudo-first order and pseudo-second order kinetics achieved from this study.

	Pseudo-first-order			Pseudo-second-order			
Adsorbate	$q_{e,\text{calculated}}$ (mg/g)	K_1 (L/min)	R^2	$q_{e,\text{experimental}}$ (mg/g)	$q_{e,\text{calculated}}$ (mg/g)	K_2 (g/mg.min)	R^2
EBT	66.35	0.227	0.96	79.88	76.44	0.122	0.99

The experimental data of EBT removal were also explored by pseudo-second-order model. The kinetic model assumes that adsorption process of EBT on the surface of HDTMA-modified MC is chemisorption. The pseudo-second-order kinetic model is represented by the following equation:

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

where K_2 (g/mg.min, the rate constant of the pseudo-second-order model) and q_e were obtained from the intercept and gradient of t/q_t versus t, respectively.

Table 3 shows the amounts of kinetic parameters of EBT adsorption by HDTMA-modified MC. As is obvious in Figure 5, the pseudo-first-order kinetic model has a value of the correlation coefficient ($R^2 > 0.96$) less than of pseudo-second-order kinetic model ($R^2 > 0.99$). Furthermore, the calculated q_e for pseudo-second-order kinetic is closer to experimentally obtained q_e at equilibrium state. Thus, the adsorption process of EBT as an azo dye by HDTMA-modified MC well followed by the pseudo-second-order kinetic model, which shows the process is chemisorption controlled.

Similar kinetic results were expressed for the uptake of EBT onto other adsorbents such as $NiFe_2O_4$ magnetic nanoparticles (Moeinpour *et al*. 2014) and Scolymus hispanicus (Barka *et al*. 2011).

3.6. Effect of adsorbent dosage

Figure 6(a) illustrates the influence of adsorbent dosages (1–10 g/L of the solution) on the adsorption

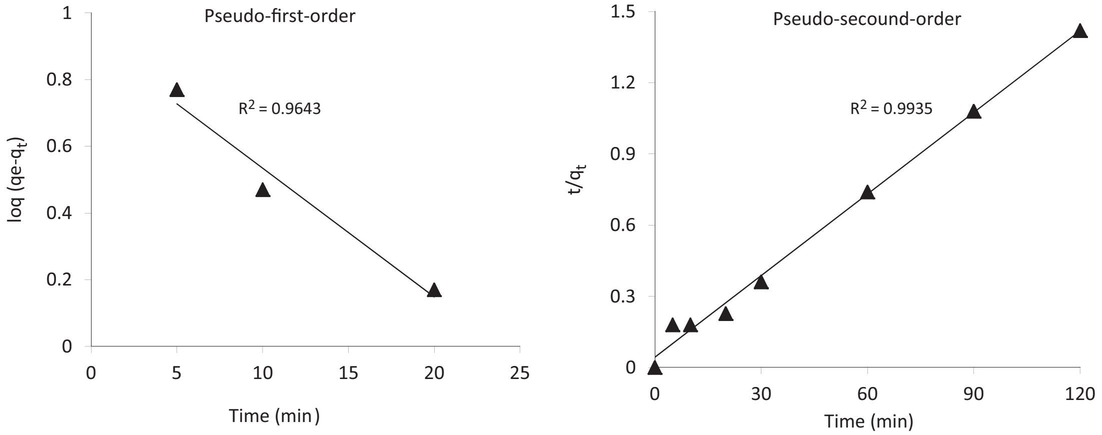


Figure 5. Comparison of various adsorption capacities of EBT removal.

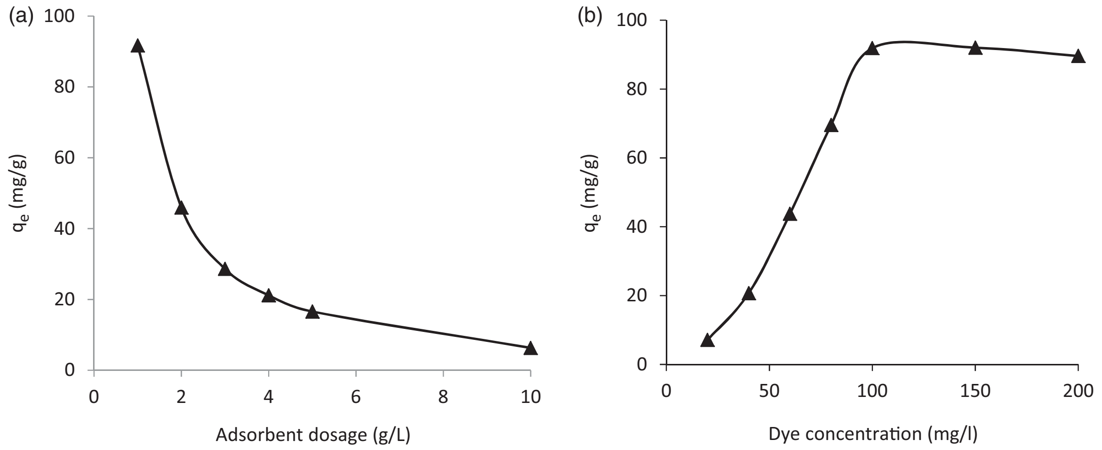


Figure 6. (a) Effect of adsorbent dosage on EBT adsorption (contact time = 30 min, concentration of EBT = 100 mg/L, pH = 3) and (b) effect of adsorbate concentration (contact time = 30 min, pH = 3, adsorbent dose = 1 g/L).

of EBT from aqueous solutions. As is obvious, the adsorption capacity of HDTMA-modified MC was rapidly decreased from 93 mg/g to 6.38 mg/g by increasing in adsorbent dosage from 1 g to 10 g per liter of the dye solution. Fourest and Roux (1992) expressed that a decrease in adsorbent concentration at a stated level of pollutant results in an increase of the adsorbate/adsorbent ration, thus enhances the adsorption capacity of the sorbent (Fourest and Roux 1992). Reducing the adsorption rate of EBT at the upper HDTMA-modified MC dosages may be due to the less accessibility of the adsorbent active sites resulted from gathering and overlapping the adsorbent particles. In order words, this phenomenon that happened in the higher content of the adsorbent caused to reduce of dye molecules uptake onto the HDTMA-modified MC. Therefore, the remainder experiments were performed by 1 g/L of the HDTMA-modified MC dosage.

3.7. Effect of initial EBT concentration

The effect of various initial EBT concentrations (20–200 mg/L) was assessed on the uptake of the dye by HDTMA-modified MC in contact time of 30 min, pH of 2 and adsorbent dosage of 1 g/L at 25 °C. The results of initial EBT concentration are depicted in Figure 6(b). As shown, by raising the EBT content in the solutions to 100 mg/L, the uptake value of EBT in the adsorbent surface was progressively increased to 89.83 mg/g and then reached to a fixed state for 200 mg/L. This result may be because of an increment in driving power of the dye such as Vander Waal's force to the adsorption sites of the adsorbent surface that happens at the elevated of EBT concentrations.

3.7.1. Isotherm study

In order to understanding how a molecules interact with adsorbents and how the molecules distribute between the phases of solid and liquid, when a uptake

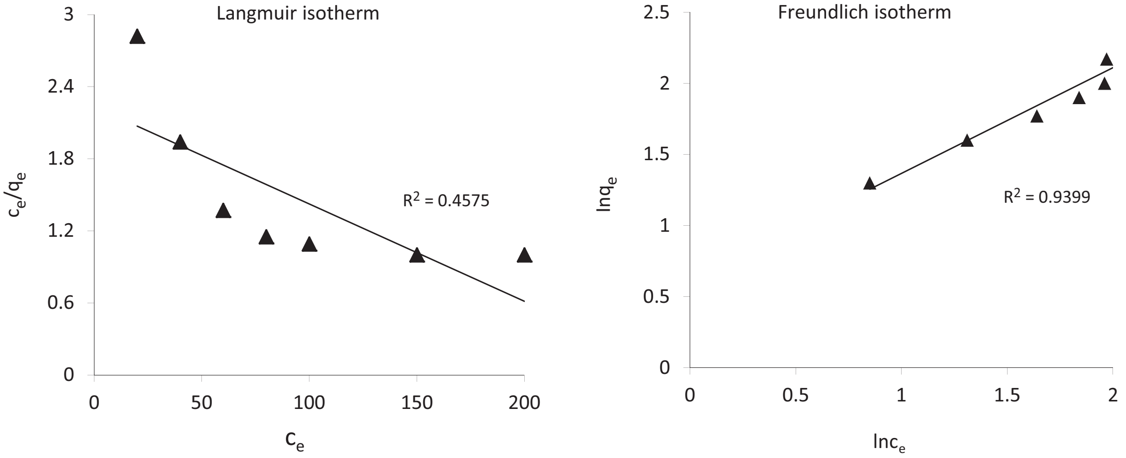


Figure 7. Plots of Langmuir and Freundlich isotherm models.

process reaches equilibrium state. Thus, it is necessary to optimize the selective adsorbent for removal of pollutants from the environment (Babaei *et al.* 2016, Khurana *et al.* 2018). The experimental data of EBT adsorption were used to determine of the isotherms. Therefore, two isotherms include Langmuir and Freundlich models were employed for this purpose. The Langmuir isotherm approximates the greatest monolayer adsorption on the uniform surface of the adsorbent (Liu *et al.* 2015). The linearized form of Langmuir isotherm is presented by the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \tag{4}$$

where C_e (mg/L) and q_e (mg/g) are the initial EBT concentration and the HDTMA-modified MC uptake capacity in the equilibrium time, respectively. Q_m (maximum sorption amount, mg/g) and b (the rate constant of Langmuir, L/mg) were acquired from the slope and intercept of linear plotting of C_e/q_e versus C_e, respectively (Yang *et al.* 2004). The maximum adsorption capacity of EBT removal by HDTMA-modified MC was found to be 321.5 mg/g. Figure 7 (left) shows the liner plot of Langmuir isotherm. The Langmuir isotherm can be depicted with a dimensionless constant separation factor, R_L, also called the equilibrium parameter that used to describe the characteristics of Langmuir adsorption isotherm. R_L was obtained from the following equation:

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

where C_0 is the maximum initial EBT concentration. The value of separation factor (R_L) shows the adsorption condition as unfavorable (R_L more than 1), liner (R_L equals to1), irreversible (R_L equals to 0), and favorable (R_L between 0 and 1). Based on the value of R_L in this study ($R_L = 0.64$), the adsorption process of EBT using HDTMA-modified MC was favorable.

Table 4. Parameters of Langmuir and Freundlich isotherms obtained from this study.

	Langmuir isotherm				Freundlich isotherm		
Adsorbate	Q_m (mg/g)	b (L/mg)	R^2	R_L	K_f (L/g)	n	R^2
EBT	321.5	0.006	0.45	0.64	0.71	1.36	0.94

The Freundlich isotherm is often expressed for multilayer adsorption onto a heterogeneous surface of the adsorbent. This isotherm model is based on this assumption which active surface sites are distributed exponentially (Wang *et al.* 2005). The linear form of Freundlich isotherm has shown by the following equation:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \tag{6}$$

where K_f (l/g) and n are the rate constants of Freundlich and depict the capability and strength of the uptake process, respectively. As shown in Figure 7 (right), the Freundlich parameters of K_f and n were achieved using the cut off and gradient of plotting ln q_e versus ln C_e, respectively.

The parameter n is the adsorption intensity, and if is more than 1 indicating the adsorption bonds between EBT and HDTMA-modified MC are appropriately powerful.

Table 4 represents the calculated values of isotherm parameters of EBT removal by HDTMA-modified MC. As seen, the value of n computed by Freundlich model is 1.36. Furthermore, the Freundlich isotherm demonstrated a higher R^2 value than Langmuir isotherm. Therefore, it has shown that the experimental data of EBT uptake onto the surface of HDTMA-modified MC was well followed by the Freundlich isotherm model. Similar results were presented for the uptake of EBT

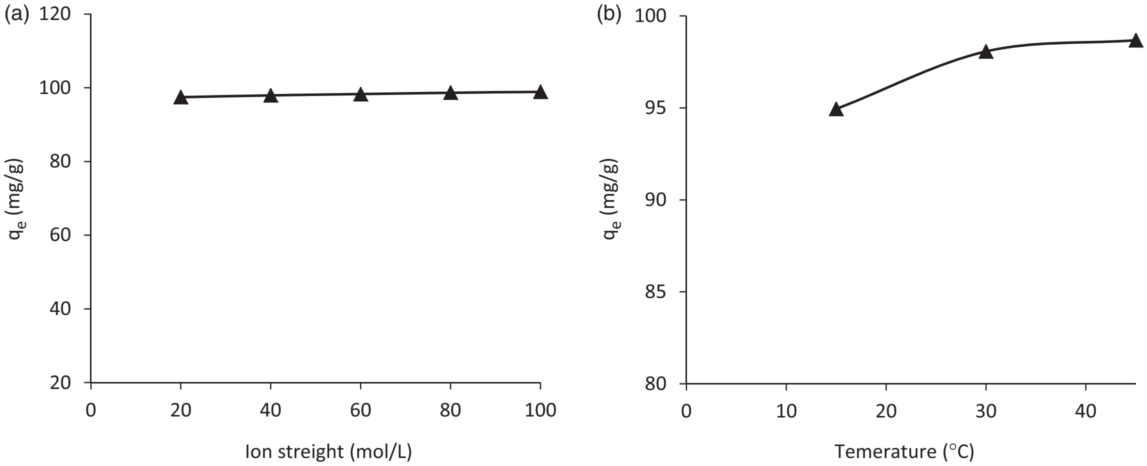


Figure 8. (a) Effect of ionic strength of solution on EBT adsorption (contact time = 30 min, EBT concentration = 100 mg/L, adsorbent dosage = 1 g/L, pH = 3) and (b) effect of temperature (contact time = 30 min, EBT concentration = 100 mg/L, adsorbent dosage = 1 g/L, pH = 3).

Table 5. Various thermodynamic parameters for the sorption of EBT by HDTMA-modified MC.

	q_e (mg/g)			ΔG (kJ/mol)			ΔH	ΔS
Adsorbate	288 K	303 K	318 K	288 K	303 K	318 K	(kJ/mol)	(J/mol K)
EBT	94.94	97.08	99.2	−57.94	−61.93	−65.74	54.5	254.47

by various adsorbents including $NiFe_2O_4$ magnetic nanoparticles (Moeinpour *et al.* 2014), modified kaolinite clay (Sonba and Ridha 2014), and Mosambi peel activated carbon (Ladhe *et al.* 2011).

3.8. Effect of solution ion strength

The purpose of investigation of the effect of solution ionic strength in the adsorption system is important because these aqueous suspensions typically have the different level of salt ions. $CaCl_2$ was used as a model salt to the study of electrolyte content effect on the removal of EBT by HDTMA-modified MC. The adsorption study in this stage was carried out by adding different amounts of calcium chloride, $CaCl_2$ (20–100 mol/l of Ca^{2+} ions) into 100 mL dye solution (100 mg/L) containing 1 g/L HDTMA-modified MC in contact time of 30 min and pH equal to 3 at room temperature. As shown in Figure 8(a), the solution ion strength had not a significant effect on the increase/or decrease of the adsorption capacity of HDTMA-modified MC. By increasing the solution ion strength even in the presence of 100 mg/L resulted in negligible changes in EBT removal by HDTMA-modified MC. This result illustrated that HDTMA-modified MC can be effectively employed to remove of EBT azo dye from low to high ionic strength aqueous solutions. These results are similar to the results of Nourmoradi *et al.* (2015) for the removal of methylene blue and acid orange 7 by AC-ZnO from aqueous solutionset *al.*

3.9. Effect of temperature

The amounts of EBT adsorption onto HDTMA-modified MC were determined at different temperatures from 15 to 45 °C and the results are shown in Figure 8(b). The equations of (7)–(10) were used to designate the thermodynamic parameters including enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS):

$$\Delta G = -RT \ln k \tag{7}$$

$$k = \frac{q_e}{C_e} \tag{8}$$

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

$$\ln k = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{10}$$

where enthalpy (kJ/mol) and entropy (J/k mol) of the adsorption system were attained from the intercept and slope of plot of ln *k* versus T^{-1}, respectively.

The quantities of all the thermodynamic parameters are demonstrated in Table 5. As can be obvious, the values of Gibbs free energy were negative. The negative quantities of ΔG imply that the adsorption system was thermodynamically practical and spontaneous. The Gibbs free energy also shows that the adsorption system was physical in nature. The uptake capacity of HDTMA-modified MC in the removal of EBT was increased by increasing the temperature from 288 to 318 K. These results revealed that the adsorption process of EBT was endothermic. Moreover, the positive value of enthalpy has also confirmed this fact.

Table 6. Comparison of various adsorption capacities of EBT removal.

Adsorbent	EBT conc. (mg/L)	Equilibrium time (min)	Adsorption capacity (mg/g)	Ref.
Magnetic graphene oxide	10.14	300	85.46	Khurana *et al.* (2018)
$NiFe_2O_4$ magnetic nanoparticles	10	10	7.02	Moeinpour *et al.* (2014)
Mosambi peel activated carbon	100	120	46.50	Sonba and Ridha (2014)
Waste rice hulls activated carbon	95	60	2.28	de Luna *et al.* (2013)
Bentonite carbon composite	50	40	2.89	El-Dars Ibrahim *et al.*
H_3PO_4-modified-berry leaves	100	60	133.33	Ahmaruzzaman *et al.* (2015)
H_2SO_4 modified clay	100	60	16.50	Elijah and Nwabanne (2014)
HDTMA-modified MC	100	30	83.01	This study

3.10. Comparison with other studies

A comparison between the results of our study with other conducted researches on the removal of EBT by various adsorbents is presented in Table 6. As is obvious, the adsorption capacity (q_e, mg/g) of HDTMA-modified MC in equilibrium time is almost higher than other adsorbents (except magnetic graphene oxide and H_3PO_4 modified-berry leaves). The results of the table show HDTMA-modified MC have a high adsorption capacity for EBT toward other adsorbents.

4. Conclusions

In this study, in a batch system, the surface of montmorillonite clay (MC) was modified by cationic surfactant of hexadecyl trimethyl ammonium bromide (HDTMA) and then applied as a low-cost adsorbent for the removal of Eriochrome black T (EBT) from aqueous solutions. The adsorption capacity was reached to equilibrium (83.01 mg/g) in contact time of 30 min. The optimum solution pH was found to be at pH 3. The results illustrated that the experimental data of EBT adsorption onto the HDTMA-modified MC surface as adsorbent were best fitted by the pseudo-second-order kinetic and Freundlich isotherm models. The solution ion strength based on mol/L Ca^{2+} ions does not have a significant effect on the adsorption capacity of EBT. Thermodynamic parameters also revealed that the adsorption process was thermodynamically feasible and spontaneous as well as was physical in nature. Moreover, the results showed that the HDTMA-modified MC had a great EBT uptake capability.

Disclosure statement

All authors declare that there is no conflict of interest in this study.

Funding

The authors would like to thank the Vice Chancellery for Research of Lorestan University of Medical Sciences for financial supporting of this study [Grant no. LUMS-1615].

References

Ahmadi, M., *et al*., 2016. A novel catalytic process for degradation of bisphenol A from aqueous solutions: a synergistic effect of nano-Fe_3O_4@ Alg-Fe on O_3/H_2O_2. *Process safety and environmental protection*, 104, 413–421.

Ahmaruzzaman, M., Ahmed, M.J.K., and Begum, S., 2015. Remediation of Eriochrome Black T-contaminated aqueous solutions utilizing H3PO4-modified berry leaves as a non-conventional adsorbent. *Desalination and water treatment*, 56 (6), 1507–1519.

Alex, A.S., *et al*., 2017. Effect of organically modified montmorillonite clay on the properties of hydroxyl terminated polydimethyl siloxane. *Journal of adhesion science and technology*, 31 (13), 1496–1513.

Arfi, R.B., Karoui, Mougin, S.K., and Ghorbal, A., 2017a. Enhanced Removal of Eriochrome Black T from Water Using Phragmites Australis Functionalized with Cetyltrimethylammonium Bromide (CTAB). Euro-Mediterranean Conference for Environmental Integration, Springer.

Arfi, R.B., Karoui, Mougin, S.K., and Ghorbal, A., 2017b. Tunisian Almond Shell for Efficient Removal of Eriochrome Black T and Malachite Green Dyes from Aqueous Solution. Euro-Mediterranean Conference for Environmental Integration, Springer.

Babaei, A.A., *et al*., 2016. Optimization of cationic dye adsorption on activated spent tea: equilibrium, kinetics, thermodynamic and artificial neural network modeling. *Korean journal of chemical engineering*, 33 (4), 1352–1361.

Basiri, H., *et al*., 2015. Removal of aniline as a health-toxic substance from polluted water by Aloe vera waste-based activated carbon. *Der pharma chemical*, 7, 149–155.

Biglari, H., *et al*., 2018. Cationic surfactant-modified clay as an adsorbent for the removal of synthetic dyes from aqueous solutions. *International journal of chemical reactor engineering*, 20170064.

Barka, N., Abdennouri, M., and Makhfouk, M.E., 2011. Removal of methylene blue and Eriochrome Black T from aqueous solutions by biosorption on Scolymus hispanicus L.: kinetics, equilibrium and thermodynamics. *Journal of the Taiwan institute of chemical engineers*, 42 (2), 320–326.

Cheng, Q., *et al*., 2017. Effects of low-dose zearalenone-contaminated diets with or without montmorillonite clay adsorbent on nutrient metabolic rates, serum enzyme activities, and genital organs of growing-laying hens. *The journal of applied poultry research*, 26 (3), 367–375.

Dave, P.N., Kaur, S., and Khosla, E., 2011. Removal of Eriochrome black-T by adsorption on to eucalyptus bark using green technology. *Indian journal of chemical technology*, 18, 53–60.

de Luna, M.D.G., *et al.*, 2013. Adsorption of Eriochrome Black T (EBT) dye using activated carbon prepared from waste rice hulls—optimization, isotherm and kinetic studies. *Journal of the Taiwan institute of chemical engineers*, 44 (4), 646–653.

Djomgoue, P., *et al.*, 2012. Surface modification of Cameroonian magnetite rich clay with Eriochrome Black T. Application for adsorption of nickel in aqueous solution. *Applied surface science*, 258 (19), 7470–7479.

El-Dars, F.M., *et al.*, 2015. Adsorption kinetics of bromophenol blue and eriochrome black t using bentonite carbon composite material. *International journal of scientific & engineering research*, 6 (5), 679–688.

Elijah, O.C. and Nwabanne, J., 2014. Adsorption studies on the removal of Eriochrome black-T from aqueous solution using Nteje clay. *SOP transactions on applied chemistry*, 1, 14–25.

Elmoubarki, R., *et al.*, 2015. Adsorption of textile dyes on raw and decanted Moroccan clays: kinetics, equilibrium and thermodynamics. *Water resources and industry*, 9, 16–29.

Fourest, E. and Roux, J.-C., 1992. Heavy metal biosorption by fungal mycelial by-products: mechanisms and influence of pH. *Applied microbiology and biotechnology*, 37 (3), 399–403.

Khaniabadi, Y.O., *et al.*, 2017. Adsorption of Congo Red Dye from aqueous solutions by montmorillonite as a low-cost adsorbent. *International journal of chemical reactor engineering*, 16. DOI:10.1515/ijcre-2016-0203

Khaniabadi, Y.O., *et al.*, 2016. Low-cost sorbent for the removal of aniline and methyl orange from liquid-phase: Aloe Vera leaves wastes. *Journal of the Taiwan institute of chemical engineers*, 68, 90–98.

Khattri, S. and Singh, M., 2009. Removal of malachite green from dye wastewater using neem sawdust by adsorption. *Journal of hazardous materials*, 167 (1), 1089–1094.

Khurana, I., *et al.*, 2018. Batch and dynamic adsorption of Eriochrome Black T from water on magnetic graphene oxide: experimental and theoretical studies. *Journal of environmental chemical engineering*, 6 (1), 468–477.

Krishna, B., Murty, D., and Prakash, B.J., 2001. Surfactant-modified clay as adsorbent for chromate. *Applied clay science*, 20 (1), 65–71.

Ladhe, U., *et al.*, 2011. Adsorption of erichrome black T from aqueous solutions on activated carbon prepared from mosambi peel. *Journal of applied sciences in environmental sanitation*, 6 (2), 149–154.

Lian, L., Guo, L., and Guo, C., 2009. Adsorption of Congo red from aqueous solutions onto Ca-bentonite. *Journal of hazardous materials*, 161 (1), 126–131.

Lin, L., *et al.*, 2013. Dye adsorption of mesoporous activated carbons produced from NaOH-pretreated rice husks. *Bioresource technology*, 136, 437–443.

Liu, Q., *et al.*, 2015. Adsorption of an anionic azo dye by cross-linked chitosan/bentonite composite. *International journal of biological macromolecules*, 72, 1129–1135.

Mittal, A. and Gupta, V.K., 2010. Adsorptive removal and recovery of the azo dye Eriochrome Black T. *Toxicological and environ chemistry*, 92 (10), 1813–1823.

Moeinpour, F., Alimoradi, A., and Kazemi, M., 2014. Efficient removal of Eriochrome black-T from aqueous solution using NiFe 2 O 4 magnetic nanoparticles. *Journal of environmental health science and engineering*, 12 (1), 112.

Mohammadi, M.J., *et al.*, 2017. Montmorillonite as adsorbent for the removal of methyl red from aqueous solution. *Fresenius environmental bulletin*, 26 (6), 4088–4096.

Nourmoradi, H., Ghiasvand, A., and Noorimotlagh, Z., 2015. Removal of methylene blue and acid orange 7 from aqueous solutions by activated carbon coated with zinc oxide (ZnO) nanoparticles: equilibrium, kinetic, and thermodynamic study. *Desalination and water treatment*, 55 (1), 252–262.

Nourmoradi, H., Nikaeen, M., and Khiadani, M., 2012. Removal of benzene, toluene, ethylbenzene and xylene (BTEX) from aqueous solutions by montmorillonite modified with nonionic surfactant: equilibrium, kinetic and thermodynamic study. *Chemical engineering journal*, 191, 341–348.

Omidi-Khaniabadi, Y., *et al.*, 2016. Hexadecyl trimethyl ammonium bromide-modified montmorillonite as a low-cost sorbent for the removal of methyl red from liquid-medium. *IJE transactions A: basics*, 29 (1), 61–69.

Silva, M., *et al.*, 2012. Adsorption of an industrial anionic dye by modified-KSF-montmorillonite: evaluation of the kinetic, thermodynamic and equilibrium data. *Chemical engineering journal*, 203, 259–268.

Sonba, H.J. and Ridha, S.H., 2014. Thermodynamics of adsorption of eriochrome black-T dye from aqueous media on each modified kaolin clay and talc. *Acta chimica and pharmaceutica indica*, 4 (2), 111–118.

Su, J., *et al.*, 2011. Adsorption of phenol from aqueous solutions by organomontmorillonite. *Desalination*, 269, 163–169.

Tanzifi, M., *et al.*, 2018. Adsorption of Amido Black 10B from aqueous solution using polyaniline/SiO_2 nanocomposite: experimental investigation and artificial neural network modeling. *Journal of colloid and interface science*, 510, 246–261.

Wang, S., *et al.*, 2005. Removal of dyes from aqueous solution using fly ash and red mud. *Water research*, 39 (1), 129–138.

Yang, Y.J., Lee, C.H., and Koo, Y.M., 2004. Separation of amino acids by simulated moving bed using competitive Langmuir isotherm. *Biotechnology and bioprocess engineering*, 9 (5), 331–338.

Zhang, S., *et al.*, 2017. Thermodynamic mechanism and interfacial structure of kaolinite intercalation and surface modification by alkane surfactants with neutral and ionic head groups. *The journal of physical chemistry C*, 121 (16), 8824–8831.

Zhang, Z.Z., Sparks, D.L., and Scrivner, N.C., 1993. Sorption and desorption of quaternary amine cations on clays. *Environmental science & technology*, 27 (8), 1625–1631.

Zubair, M., *et al.*, 2017. Adsorption of eriochrome black T from aqueous phase on MgAl-, CoAl-and NiFe-calcined layered double hydroxides: kinetic, equilibrium and thermodynamic studies. *Journal of molecular liquids*, 230, 344–352.