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Investigation of the adsorption of Astrazon Blue FGRL dye in synthetic wastewater using waste mine clay

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Abstract

In this investigation is aimed at the removal of Astrazon Blue FGRL (AB FGRL) (basic dye) from an aqueous solution using waste clay (MC) obtained from the gold mine area. The natural clay was characterized and identified using X-ray diffraction (XRD) analysis.Then, the contact time, adsorbent dosage, pH, initial dye concentration and temperature experiments were carried out in a batch system. The removal efficiency was found to be 97% at pH 7, 80 min, 30ºC, 4 g/L MC dosage, 50 mg/L initial dye concentration. The adsorption data are applied to the Langmuir, Freundlich, and Temkin isotherm models. The maximum capacity of waste mine clay (MC) was found to be 191.75 mg/g. The pseudo-second-order kinetic models and Elovich kinetic model were used to examine the adsorption process of Astrazon Blue FGRL. The results of kinetic experiments were defined by the pseudo-second-order model point out a chemisorption reaction. The adsorption thermodynamics were investigated using parameters such as enthalpy change (ΔH^o), Gibbs free energy change (ΔG^o) as well as entropy change (ΔS^o). These calculations reveal that sorption of Astrozon Blue FGRL is endothermic, spontaneous and enthalpy driven. This work provides guidance for using of waste clay materials for applications in the adsorption removal of dye from aqueous solution.

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1. Introduction

The textile industry has used large amounts of water and chemicals in various processing stages for instance sizing, washing, decolorant, mercerizing, coloring, printing, and finishing [1]. The wastewater generated from the textile industries contains different types of dyes that are very low biodegradable due to complex structures and high molecular weight [2]. The cationic textile dyes are basic dyes which are synthetic pigments and are widely used in the textile industry. These dyes belonging to the cationic basic dye group are water-soluble. The basic dyes have often used in several processes for example acrylic, nylon, silk, and wool coloring [3]. The performance of the coloring process is often poor, causing large amounts of dye to escape from the wastewater. Dumping into the water bodies from no treatment of dye-bearing wastewaters has posed a danger to human health, aquatic living, and water quality, thus becomes vital importance [4]. Discharge of wastewater containing dyes into natural receiving environments such as streams and rivers have a great influence on the photosynthetic activity in aquatic organisms and exhibit a low biodegradability [5]. It also damages the aesthetic structure of the environment and causes health problems for people such as skin irritation, cancer, mutation, allergic dermatitis [6]. The treatment obligation of dye wastewater, relevant industries need to treat wastewater containing dyes before discharging them into a body of water.

Many treatment techniques for example chemical coagulation [1], biodegradation [7], membrane separation [8], electrocoagulation [9], Fenton process [10], ozone oxidation [11], electrochemical degradation [12], ultrasonic degradation [13], photo-catalytic oxidation [14], and adsorption techniques [15] have been applied for the removal of textile wastewater. Adsorption is a prime wastewater treatment method for dyes removal due to its simplicity of design, non-generation of toxic materials, low cost and high efficiency [16]. Generally, activated carbon is the most common adsorbent that commonly utilized for treatment of wide range of water pollutants [17]. However, its initial cost, rapid saturation and difficult in regeneration make it less attractive as an adsorbent. [18, 19]. Therefore, in recent years, studies have

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focused on the development of cost effective and environment friendly adsorbents. Various low-cost adsorbents have been proposed by numerous researchers, containing natural materials, waste materials, and biosorbents, from agriculture and industry processes [4, 6, 20-22]. The sorbents are used in other studies are clay materials (kaolinite, bentonite), siliceous materials (alunite, silica beads, perlite), zeolites, agricultural waste (corncob, pulp, nutshells, rice husk, almond shell, coconut shell), products of the industrial waste (red sludge, compost industry waste, blast furnace sludge, and fly ash), biosorbents (chitosan, biomass, peat) and others (cyclodextrin, starch, chitosan). These materials can be used as absorbents for removing cationic, anionic, and reactive dyes from aqueous solutions. The utilization of natural clays as alternative adsorbents for the removal of dyes from wastewater offers several advantages such as low-cost, high adsorption properties, porosity, availability, thermal stability, large potential for ion exchange, plenty in most landmasses worldwide and nontoxicity [23]. The strong adsorption capabilities of clay minerals are related to the negative charge in the structure of grain silicate minerals. This negative charge can be neutralized by adsorption of positively charged cations such as dyes. [24].

The aim of this study is to provide dye removal from wastewater and to investigate the reusability of wastes by using waste material. In addition, the reuse of waste materials is an environmentally friendly approach. For this porpose, the use of waste mine clay (MC) from the gold mine area as an effective adsorbent for the treatment of Astrazon Blue FGRL (basic dye) from an aqueous solution was evaluated. Adsorption experiments were applied under various operational parameters such as contact time, adsorbent dosage, solution pH, initial dye concentration and temperature. Adsorption kinetic data were verified with the so-called pseudo-second-order kinetic model and Elovich equation model. Equilibrium data were calculated using the Langmuir, Freundlich, and Temkin isotherm models. Also, the adsorption thermodynamics were calculated.

2. Materials and Methods

2.1. Waste clay and dye characterization

Waste mine clay (MC) was collected from a gold mine area in Sivas, Turkey, and XRD spectrum is as follows (Figure 1). The MC was crushed and dried followed by in a hot air oven at 80 °C for 48 h before use.

Astrazon Blue FGRL used for the study was supplied from Dystar, Turkey. This dye contains two main dyes, including C.I. Basic Blue 159 and C.I. Basic Blue 3. The ratio of the two dyes is 5:1 (w/w), respectively, and the structures of two dye components are presented in Figure 1 [25]. The basic dye is mostly used as acrylic painting in the industry [26]. This dye has not intensely toxic, nonetheless could cause short-term rapid or difficult breathing when inhaled [26].

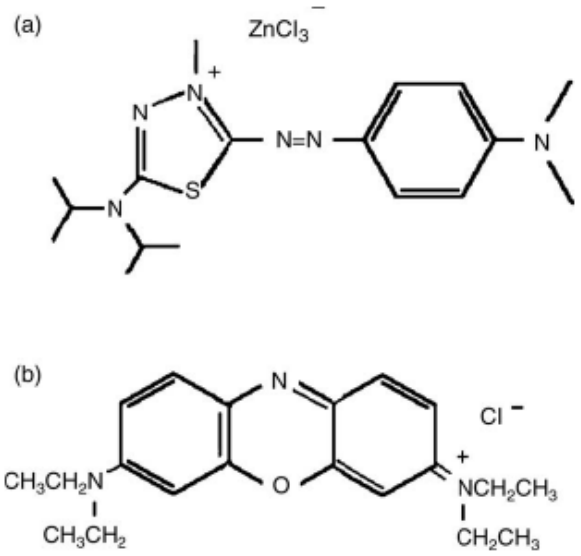

Figure 1. Chemical structure of AB FGRL ((a) C.I. Basic Blue 159 and (b) C.I. Basic Blue 3).

2.2. Adsorption experiments

All batch adsorption tests were completed in 100 mL Erlenmeyer and 50 mL solution volume in a shaker unit with a thermostat at 300 rpm. Influences of contact time, adsorbent dosage, solution pH, initial dye concentration and temperature were studied. In this study, samples were taken over time to measure the dye concentration residual in the aqueous solution. The influence of varying contact time (5-80 min) was studied at 100 ppm Astrazon Blue FGRL dye concentrations, adsorbent dosage (0.5-1-2 g/L), pH 7.0 and 30 °C. The influence of MC dosage on removal of Astrazon Blue FGRL dye was tested by varying adsorbent dosage from 0.5 to 10 g/L in initial dye concentration (100-200-400-600 and 800 mg/L) at pH 7.0 and 30 °C for contact time 1440 min. The influence pH was studied different pH values as 5, 7, 9 and 12 at MC dosage 4 g/L for different contact time (5-10-15-20-30-40-60-80 min). The initial pH of the dye aqueous solution was adjusted using HCl and NaOH solutions. The influence of different initial dye concentrations (50-100-200-400-600-800 mg/L) was carried out by in for contact time 80 min at pH 7.0 and 30 °C. Thermodynamic adsorption experiments were performed in a shaker water bath (GFL model 1086) at 30, 40 and 60 °C. At the end of the experiment, solid-liquid separation was made by centrifugation at 4000

rpm for 20 min. Thus, the final dye concentration in the supernatant was determined. The amount of dye (qe, mg/g) adsorbed on the adsorbent at equilibrium was calculated as follows (Eq. 1):

$$q_e = \frac{(C_o - C_e)V}{m_s} \quad (1)$$

where Co and Ce are dye concentrations in solution at the initial time and equilibrium, respectively (mg/L); V, is the volume of the dye solution (L); m_s, is the mass of the adsorbent or MC (g). The removal efficiency (R_e,%) of Astrazon Blue FGRL by the adsorbent was calculated as follows (Eq. 2):

$$R_e = \frac{(C_o - C_t)}{C_o} x100 \quad (2)$$

2.3. Analytical methods

The concentration of the Astrazon Blue FGRL solution was determined using a UV/vis spectrophotometer (Merck, Pharo 300 Model, German) with a detecting wavelength at 576 nm. The pH of the dye solution was measured with a pH meter (WTW Inolab Multi 9310 IDS) using a combined glass electrode. All chemical reagents used are of analytical grade and are prepared in Millipore Milli-Q deionized water. All experiments were done twice and the experimental error was less than 1%.

2.4. Kinetic modeling, isotherm and thermodynamic parameters

The pseudo-second-order adsorption kinetic rate equation is given as (Eq. 3) [27]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \quad (3)$$

The plot of *t/qt* and *t* should give a linear relationship from which *qe* and k_2 can be determined from the slope and intercept of the plot, respectively. This equation is the initial adsorption rate (h) (Eq. 4);

$$h = k_2 q_e^2 \quad (4)$$

The Elovich model equation is commonly expressed as (Eq. 5) [28]:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (5)$$

where: α is the initial adsorption rate ($mg.g^{-1}.min^{-1}$), β is the desorption constant ($g.mg^{-1}$) during any one experiment.

The equilibrium data were analysed using Langmuir, Freundlich and Temkin isotherm models (Eq. 6, 7 and 8) [29,30].

Langmuir isotherm:

$$q_e = \frac{Q_o b C_e}{1 + bC_e} \quad (6)$$

where Q_o (mg/g) is the maximum adsorption capacity and b (L/mg) is the Langmuir constant.

Freundlich isotherm:

$$q_e = k_F C_e^{\frac{1}{n}} \quad (7)$$

where k_F (L/g) is the adsorption diffusion coefficient and represents the quantity of adsorbed dye on the adsorbent surface per unit equilibrium concentration, the other Freundlich constant 1/n represents the adsorption intensity or surface heterogeneity.

Temkin isotherm:

$$q_e = \frac{RT}{bt} \ln K_T + \frac{RT}{bt} \ln C_e \quad (8)$$

where K_T (L/g) is the isotherm constant, bt (kJ/mol) is the constant relating to sorption energy, R is 8.314 kJ $mol^{-1}K^{-1}$, and T temperature (K). According to the Temkin isotherm model, the adsorbate interacts with each other and the sorption energy in the layers decreases linearly with the coating of the adsorbate. By plotting qe versus lnC_e, a straight line is obtained by which K_T and bt can be measured.

Thermodynamic parameters such as changes in Gibbs free energy ΔG^o (kJ mol^{-1}), as well as enthalpy ΔH^o (kJ mol^{-1}) and entropy ΔS^o (J $mol^{-1}K^{-1}$) were determined by using the following equation (Eq. 9 and 10) [31].

$$\ln Kc = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (9)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (10)$$

where R is gas constant (8.314 kJ $mol^{-1}K^{-1}$) and T is reaction temperature (K).

3. Results and Discussion

3.1. Characterization of waste clay by XRD

The spectroscopic analysis performed by the X-ray diffractometer of the wastel clay used is represented in Figure 2.

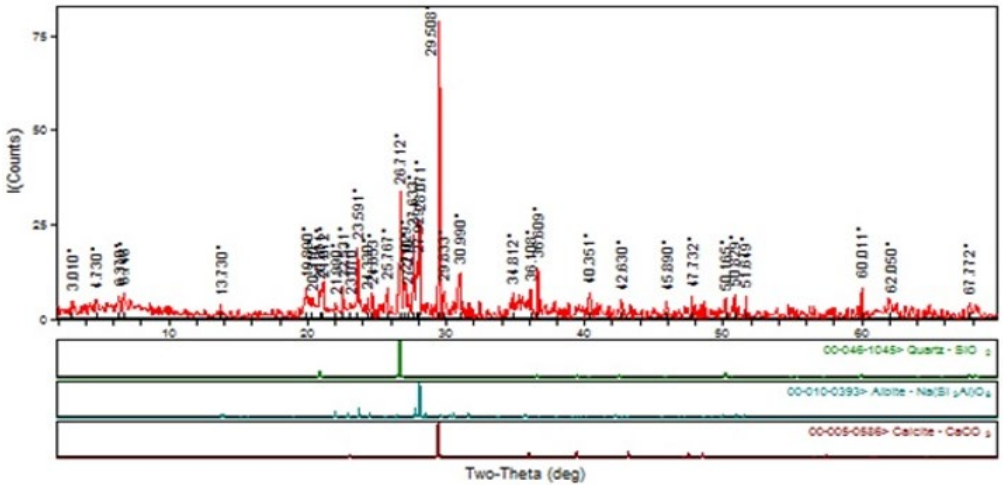

Figure 2. XRD spectrum of waste clay

From Figure 2, many diffraction peak at 2θ range 20°-30° can be observed. These results indicate the presence of Quartz, Albite and Calcite in the structure of waste clay.

3.2. Influence of contact time and MC dosage on the adsorption process and adsorption kinetics

Figure 3 represents the influence of contact time and MC dosage on the Astrazon Blue FGRL adsorption. According to Figure 3(a), the adsorption capacity slows down at longer contact times and it reaches equilibrium. In general, at the start of the experiment, the adsorption is rapid and during this phase the quantity of dye adsorbed is high. During the stationary phase, although the contact time increases the amounts of dye adsorbed by the clay are small. This can be explained during the first phase by the increased binding of dye molecules on the clay surface studied while the stationary phase is explained by the saturation of the binding sites [32, 33].

The adsorption capacity decreased when the MC dosage was increased. In this case, the high surface area and/or adsorption active sites available for adsorption of Astrazon Blue FGRL dye molecules may occur [23]. This, in turn, is thought to increase the efficiency and capacity of Astrazon Blue FGRL. Further increase in MC dosage above 4 g/L did not show any further improvement in Astrazon Blue FGRL dye removal. Therefore, optimum MC dosage was chosen to be 4g/L for studies the influence of pH and initial dye concentration.

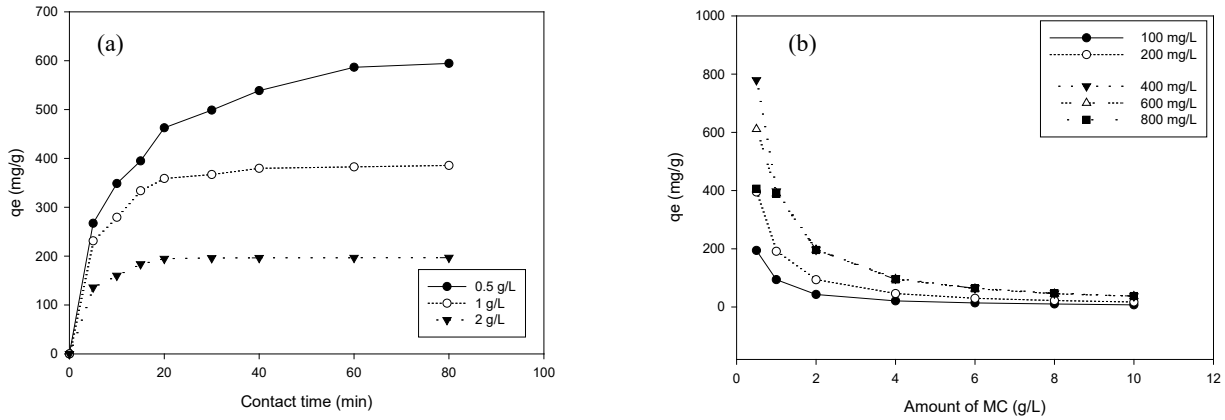

Figure 3. Influence of contact time (a) (m_s=0.5-1-2 g/L, Co= 400 mg/L, t=5-10-15-20-30-40-60-80 min, T= 30 °C, pH=7) and adsorbent dosage (b) (m_s=0.5-1-2-4-6-8-10 g/L, Co=100-200-400-600-800 mg/L, t=1440 min, T= 30 °C, pH=7) and on the adsorption process

The adsorption kinetic model constants and r^2 values are given in Table 1. Correlation coefficients of the pseudo second-order kinetic model is relatively greater than that of the Elovich kinetic model and the $q_{e,teo}$ values fitted well compliance with the $q_{e,exp}$ values, in this case, the rate-determining step can be surface adsorption. Based on the assumption of the pseudo-second-ordermodel it can be concluded that the adsorption of Astrazon Blue FGRL onto MC was chemisorption involving exchange or sharing of electrons between adsorbent and adsorbate [19, 24, 34, 35].

Table 1. The kinetic models of the Astrazon Blue FGRL adsorption in the different MC dosages

		The Pseudo second-order kinetic				The Elovich kinetic		
m_s (g/L)	$q_{e,exp}$ (mg/g)	k_2 (g/mg.min)	$q_{e,teo}$ (mg/g)	h (mg/g.min)	r^2	α (mg/g min)	β (g/mg)	r^2
0.5	614.376	$2.51x10^{-4}$	632.91	100.54	0.988	1.683	$8.02x10^{-3}$	0.985
1.0	385.609	$1.02x10^{-3}$	398.41	161.91	0.998	1.932	$17.71x10^{-3}$	0.858
2.0	196.854	$3.96x10^{-3}$	200.80	159.67	0.999	2.132	$46.63x10^{-3}$	0.738

3.2. Influence of initial solution pH on the adsorption process

Solution pH plays an important role in the sorption process. It appears to interrupt the solution chemistry of dyes and functional groups of the adsorbents. Adsorption capacity of dye depends on pH of the solution [36]. The influence of the solution pH on the Astrazon Blue FGRL adsorption was studied at initial pH values of 5–12. The adsorption capacity of Astrazon Blue FGRL was high at pH 5, 7 and 9 values (Figure 4). It was observed from Figure 4 that the increasing in solution pH from 5 to 12 the adsorption capacity, qe (mg/g) decreases from 97.96 mg/g to 90.11 mg/g for equilibrium time 30 min. Hence there was a significant change in adsorption capacity at especially pH 12. The adsorption capacity depends on the relationship of dye molecules with the surface of the adsorbent. The high adsorption capacity of the Astrazon Blue FGRL at acidic and neutral pH could be based on the cation exchange and H-bonding interactions among that can be occurred between H atom available on the MC surface and N atom in the Astrazon Blue FGRL dye structure.

$MC\text{-}SiO^- + H^+$ (solution pH) $\leftrightarrow$ $MC\text{-}SiO^-\text{-}H^+$ (electrostatic attraction)
$MC\text{-}SiO^-\text{-}H^+$ + Astrazon Blue FGRL $\leftrightarrow$ $MC\text{-}SiO^-$- Astrazon Blue FGRL + H^+ (cation exchange)

These results indicate that pH values were a limiting factor in high dye removal, pH control is necessary. The adsorption capacity of Astrazon Blue FGRL increased until 30 min contact time and at longer contact times, the adsorption rate reached equilibrium. Therefore, pH 7 was determined to be the best solution pH for the further applications.

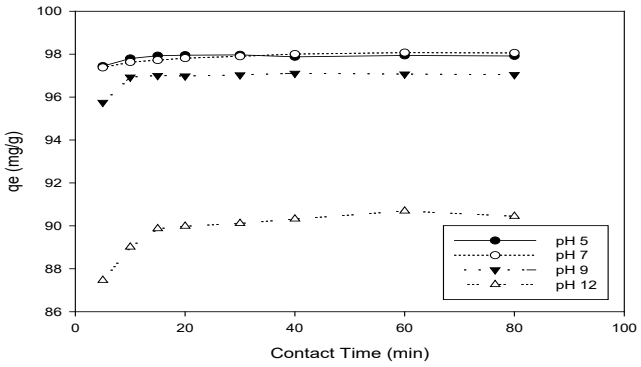

Figure 4. Influence of solution pH on adsorption process (C_o=400 mg/L, m_s=4g/L, t=5-10-15-20-30-40-60-80 min, T=30°C).

3.3. Influence of initial dye concentration on the adsorption process

The influence on the adsorption capacity of the initial Astrazon Blue FGRL concentration is demonstrated in Figure 5. The adsorbed dye amount increased when the concentration Astrazon Blue FGRL (to 147.9 mg/g from 12.18 mg/g) was increased.

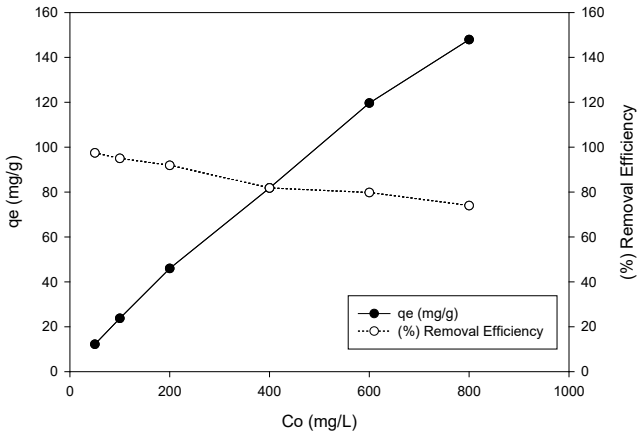

Figure 5. Influence of the initial dye concentration on adsorption process (Co=50-100-200-400-600-800 mg/L, m_s=4g/L, t=80 min, pH=7, T=30°C).

The increases with the increasing of the initial dye concentration, this can be explained by the good diffusion of the dye molecules towards to specific surface of clay studied [32]. The initial concentration was considered to play an important role in providing the necessary driving force to overcome the force to mass transfer of Astrazon Blue FGRL between aqueous solution and solid phases [37]. It was found that the interaction between the adsorbate and the adsorbent also increases with the increase in the initial concentration. Similar output has been reported in the adsorption of congo red dye using cabbage waste powder [19].Therefore, it can be concluded that a higher initial concentration increases the adsorption

uptake of Astrazon Blue FGRL. The removal efficiency was reduced with the increase in Astrazon Blue FGRL concentration (to 73% from 97%).

3.4. Adsorption isotherms

Different isotherm models were employed to study the Astrazon Blue FGRL dye adsorption by MC. The adsorption plots and isotherm parameters are presented in Figure 6 and Table 2.

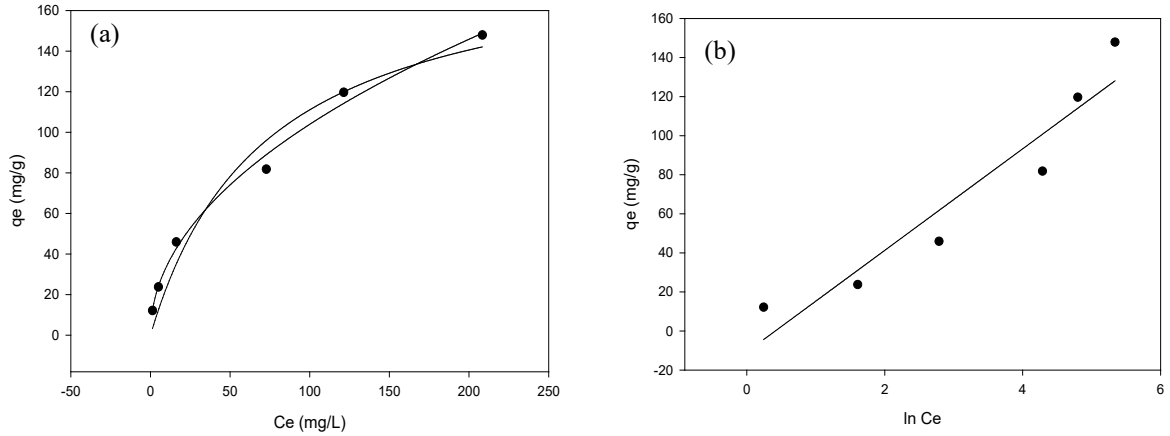

Figure 6. Langmuir, Freundlich (a) and Temkin (b) isotherm plots for Astrazon Blue FGRL adsorption

Table 2. Langmuir, Freundlich and Temkin isotherm model parameters for adsorption of Astrazon Blue FGRL dye on the MC

Langmuir Isotherm Model	MC	Freundlich Isotherm Model	MC	Temkin Isotherm Model	MC
Q_o (mg/g)	191.75	k_F (L/g)	10.9281	K_T	0.66
b (L/mg)	0.0138	1/n	0.4890	bt	96.90
r^2	0.981	r^2	0.997	r^2	0.953

According to data indicates in Table 2, Langmuir and Freundlich models are applicable and the removal efficiencies varies in the same direction according to the two models as well as the adsorption of Astrazon Blue FGRL by MC used (all r^2>0.980). It can be thought that adsorption occurs on homogeneous and heterogeneous surfaces of the adsorbent. In this case; the effect of physical and chemical adsorption can be combined [38]. The high value of the Freundlich constant (k_F; 10.9281 L/g) is associated with the high clay capacity for Astrazon Blue FGRL dye removal. The Q_o value of MC was determined as 191.75 mg/g. A comparison of Q_o values of Astrazon Blue FGRL onto various adsorbents are reported in Table 3. The results were also fitted by the Temkin model (Table 2), which suggested a reduction in the heat of adsorption along with coverage due to adsorbent-adsorbate interactions. As a result, adsorption of Astrazon Blue FGRL dye could be characterized by a uniform distribution of binding energies up to maximum value [39].

Table 3. The Q_o values obtained for adsorption of Astrazon Blue FGRL on different adsorbents

Adsorbent	Q_o (mg/g)	Reference
MC	191.75	This study
Apricot stone activated carbon	181.5	[25]
Sepiolite	155.5	[25]
Fly ash	128.2	[25]
Macroalga *C. lentillifera*	94.3	[40]
Macroalga *C. lentillifera*	49.26	[25]
Macroalga *C. lentillifera*	38.9 ± 3.4	[40]

3.5. Influence of temperature on the adsorption process and adsorption thermodynamic

The temperature is another driving force in the adsorption of Astrazon Blue FGRL dye. Temperature is known to influence the viscosity of the solution as well as controlling the rate of diffusion of the dye molecules over the external boundary layer and in the internal pores of the adsorbent [19]**.** The influence on the adsorption capacity of the temperature, and

adsorption thermodynamic plot are given in Figure 7. As seen in Figure 7, while the temperature was increased, the adsorption capacity increased. This is because at elevated temperatures, the kinetic energy of Astrazon Blue FGRL dye molecules increase which in turn increases the collision rate of the dye and MC. However, temperatures there is also a possibility of the inner pores of MC opening up increasing the adsorption sites hence high adsorption rate [19].

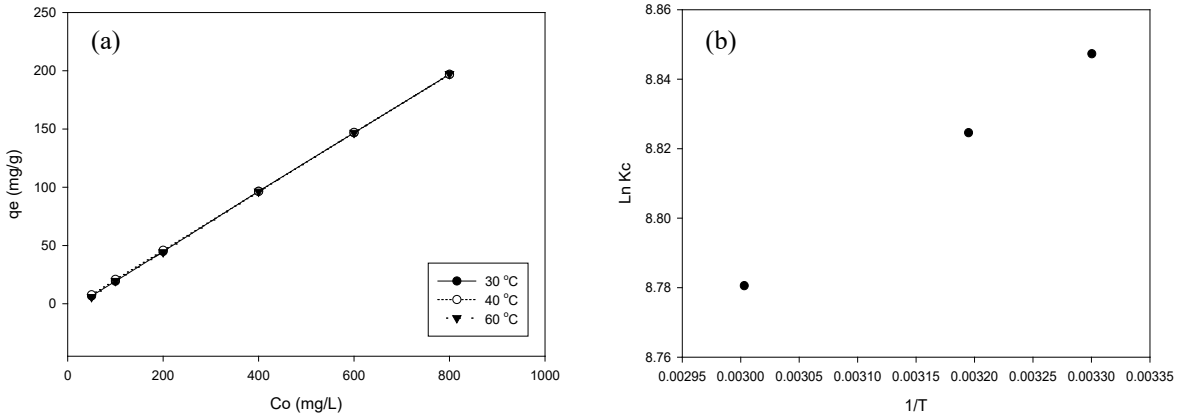

Figure 7. Influence of temperature on adsorption process (a) (Co=50-100-200-400-600-800 mg/L, m_s=4g/L, t=80 min, pH=7) and thermodynamic plot (b)

Therefore, the temperature parameter played an important role in removing Astrazon Blue FGRL from the aqueous solution. According to the thermodynamic parameters, the positive value of ΔH^o indicates that the adsorption process is endothermic (Table 4). The positive values of entropy (ΔS^o), show that randomness increased (adsorbate/adsorbent) during the adsorption process. Negative ΔG^o values indicate that adsorption is thermodynamically spontaneous and feasible. Adsorption of congo red on cabbabe waste powder showed similar trend [19].

Table 4. Thermodynamic parameters obtained for Astrazon Blue FGRL dye adsorption

	Astrazon Blue FGRL dye
ΔH^o (kJ/mol)	1.871
ΔS^o (kJ/mol.K)	67.38
ΔG^o (kJ/mol)	
303 K	-22.28
313 K	-22.96
333 K	-24.32

Conclusion

In this study, the waste clay in the gold mine region was used as an effective adsorbent for the removal of Astrazon Blue FGRL dye from aqueous solution. The amounts of adsorbed dye were calculated as a function of various parameters such as the contact time effect between clay and dye molecules, the adsorbent dosage effect, the pH of the solution, the effect of the initial dye solution concentration and solution temperature. Percent removal of Astrazon Blue FGRL dye increased with increase in contact time, temperature, dosage but dropped when pH were increased. The MC showed good sorption performance for the uptake of Astrazon Blue FGRL in various pH and concentrations. The results of the study showed that the Langmuir and Freundlich isotherms are applicable to the study of the adsorption of Astrazon Blue FGRL dye using the MC. The values of Q_o for Astrazon Blue FGRL dye at optimum conditions were 191.75 mg/g. According to the literature; the maximum adsorption capacity (Q_o) of MC for removal of Astrazon Blue FGRL dye was higher than many other adsorbents. Kinetic data were expressed by a pseudo-second-order model that demonstrates that Astrazon Blue FGRL uptake occurs by the chemisorption process. The intraparticle diffusion model confirms that the rate-determining step of adsorption is unlikely to be mass transfer diffusion. The ΔG^o and ΔS^o values obtained from thermodynamic studies showed that the adsorption process occurred spontaneously, and the feasibility and randomness increased. This study shows that MC is low-cost adsorbent, which have been successfully used for the adsorption of dye from aqueous solution on laboratory scale.

Conflicts of interest

The authors state that there is no conflict of interests.

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