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Removal of methylene blue from aqueous solution using by untreated lignite as potential low-cost adsorbent: Kinetic, thermodynamic and equilibrium approach

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ABSTRACT

The adsorption mechanism of the cationic methylene blue dye to the abundant and inexpensive lignite as an adsorbent from aqueous solutions was investigated as a function of ionic strength, pH, temperature, initial dye concentration, contact time and stirring speed. The adsorption capacity increased with the increasing temperature, initial dye concentration, pH and ionic strength, although it was not affected by the stirring speed. The value of zeta potential decreased with the increasing pH. Experimental adsorption data were modelled by different equilibrium isotherms such as Langmuir, Freundlich, Temkin, Dubinin–Radushkevich (D–R), BET, Halsey, Harkins–Jura, Smith and Henderson isotherms. The adsorption process fitted well to pseudo-second-order kinetics and the Langmuir model. Activation energy of the adsorption processes was found to be 49.81 kJ mol^{-1} initial dye concentration of 80 mg L^{-1} using the Arrhenius equation, indicating the strong electrostatic interactions between the adsorbent and dye. The isosteric enthalpy and entropy changes were calculated as 58.19 kJ mol^{-1} and −0.186 kJ mol^{-1} K^{-1}, respectively, indicating that the adsorption process was endothermic and the orderliness of the adsorption system slightly decreases with adsorption of methylene blue molecules to the lignite surface. FT-IR results revealed that several functional groups on the coal surface are responsible for methylene blue adsorption. The observed differences in the reflection of the SEM images of lignite and methylene blue adsorbed lignite are due to the presence of methylene blue, which was adsorbed. BET isotherm and nitrogen-adsorption–desorption isotherms analysis results implied that lignite is a heteroporous material exhibiting microporous properties.

1. Introduction

The discharge of dye effluents from textile, leather, paper and plastics industries into the environment poses severe problems for many forms of life. Methylene blue is the most commonly used substance for dying cotton, wood and silk [1]. Though methylene blue is not strongly hazardous, it can cause some harmful effects. Acute exposure to methylene blue can cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in humans [2]. Therefore, the removal of this dye from process effluent becomes environmentally important. Traditionally, both biological and chemical methods have been employed for dye removal, although these techniques have not been very successful due to the essentially non-biodegradable nature of most dyes [3]. All these methods have disadvantages such as incomplete removal, high reagent and energy generation of toxic sludge or other waste products that require careful disposal, high capital and operating costs, labour intensive, etc. In this light, adsorption has emerged as an efficient and cost-effective alternative to conventional contaminated water treatment facilities [4–6]. Adsorption also does not result in the formation of harmful substances.

Adsorption using carbon-based materials is a very common method for the removal of colour and organic matter from water. Although activated carbon is a preferred adsorbent, its application is often restricted due to its high cost. Cheaper, non-conventional carbon-based materials have been investigated as alternatives. Natural materials and waste materials from industry and agriculture as biosorbents have been employed as inexpensive adsorbents [7]. Many studies have treated waste materials to produce activated carbon for adsorption of organics and colour in water [8–10]. However, the treatment inevitably increases the cost of the

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materials and, therefore, of the overall process. Alternatively, non-activated coals and similar carbon-based materials, such as powdered coals [11], cattail root [12] and peat [13], have been studied as adsorbents. A significant benefit of using a low cost carbon-based material as an adsorbent is that it can still be used as a fuel, thus overcoming disposal issues.

Lignite, or brown coal, is well-known for its adsorptive properties. There have been studies using lignite as an adsorbent for the removal of not only heavy metals [14–17], but also organic pollutants and colour or dyes from wastewater [12,18–20]. In the state of Aşkale, Turkey, lignite deposits are abundant. The coal from open-cut mines is inexpensive compared to high-rank coals. The adsorptive properties of Aşkale lignite have attracted interest for its potential as an alternative adsorbent. Bayrakçeken et al. [21] investigated the adsorption of o-cresol from aqueous solutions by Aşkale brown coal-based materials and concluded that these materials were potential adsorbents for industrial and environmental applications. Nevertheless, studies on the adsorption characteristics and mechanisms of Aşkale lignite are rare. Methylene blue is one of the most commonly used model compounds for the evaluation of an adsorbent [22]. A few studies have used lignite as an adsorbent [19,22–24]. However, there have been no reports using methylene blue as a model compound to investigate the adsorption characteristics of Aşkale lignite.

The objective of the present study is to evaluate the potential of Aşkale lignite as an alternative industrial adsorbent for the removal of colour from water focusing on the characterization of the adsorbent and adsorption capacity. The present study is aimed at finding a convenient and economic method for methylene blue removal from water by adsorption on coal, to gain an understanding of the adsorption kinetics, to describe the rate and mechanism of adsorption, to determine the factors controlling the rate of adsorption and to calculate the activation energy of system. The adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were also determined. In addition, the thermodynamic activation parameters, such as enthalpy, entropy and the free energy, were also investigated to provide insights to the adsorption reactions and mechanisms.

2. Experimental

2.1. Chemicals

The coal sample used as adsorbent in this study was obtained from Aşkale coal mines in Turkey. The sample was air dried, ground and then sieved to give −180 + 400 mesh size fraction using ASTM standard sieves. Proximate and ultimate analyses were performed using Turkish and ASTM standards. The average results of duplicate analyses performed according to ASTM procedures for the coal sample are given in Table 1. As adsorbate, a cationic dye, methylene blue (Fig. 1) was chosen because it has a net positive charge which would be favourably adsorbed by electrostatic force onto a negatively charged adsorbent surface. Methylene blue ($C_{16}H_{18}N_3SCl$) is a basic blue dyestuff, CI Classification Number 52015. The aromatic moiety of methylene blue contains nitrogen and sulphur atoms. In the aromatic unit, dimethylamino groups attach to it. The aromatic moiety is planar and the molecule is positively charged. The dimensions of methylene blue molecule are16.9 Å for the length, 7.4 Å for the breadth, and 3.8 Å as thickness [25]. All chemicals used in this study were purchased from Merck and used without any further purification.

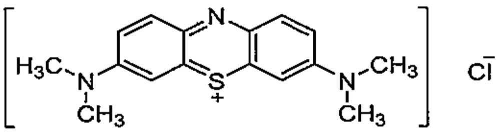

Fig. 1. Structure of methylene blue.

Table 1
Composition, oxygenated functional groups, specific surface area and heating value of studied coal Aşkale lignite.

Proximate analyses (wt.%)	Ash	29.64
	Volatile matter	34.28
	Fixed carbon	31.62
	Moisture	4.46
Ultimate analyses (wt.% daf[a])	Carbon	70.86
	Hydrogen	4.28
	Sulfur	4.76
	Nitrogen	2.20
	Oxygen (diff.)	17.90
Carboxylic groups[a]	$m_{eq}\,g^{-1}$	0.18
	wt.% O	0.58
Phenolic groups[a]	$m_{eq}\,g^{-1}$	5.57
	wt.% O	8.91
BET	N_2 ($m^2\,g^{-1}$)	38.34
Heating value	(cal/g)	5620

Results are averages of duplicate analysis (as received).

[a] Dry, ash, free basis.

2.2. Adsorption experiments

Adsorption experiments were carried out in 100 mL glass-stoppered round-bottom flasks immersed in a thermostatic shaker bath. For this, 0.15 g of coal sample was mixed with 100 mL of the aqueous solutions of various initial concentrations (10, 20, 40, 60, 80 and 100 mg L^{-1}) of methylene blue. The flasks with their contents were shaken for different adsorption times at the temperature of 293, 313 and 333 K and natural pH. The effect of pH, adsorbent dosage and stirring speed was investigated at 293 K. The initial pHs (3, 6, 7, 9, and 11) of the solutions were adjusted with concentrated HCl and NaOH solution and measured using a WTW inoLab pH metre (WTW Inc., Weilheim, Germany). The pH metre was standardized with buffers before every measurement. The effect of ionic strength on methylene blue adsorption were investigated using three electrolytes, NaCl, $CaCl_2$ and $AlCl_3$, at three different concentrations (0.01, 0.02 and 0.03 mol L^{-1}) at 293 K for 60 min. At the end of each adsorption period, the flask contents were divided into two parts. One part was passed through Whatman 40 filter paper and the filtrate was centrifuged. The second part of the coal/water suspension was used for zeta potential and electrical conductivity measurements. In the experiments, the stirring speed was kept constant at 150 min^{-1} (except for the experiments in which the effect of stirring speed was examined). At the end of adsorption period, the supernatant was centrifuged for 5 min at 6000 min^{-1}. The concentration of methylene blue in the supernatant solution before and after adsorption was determined with a 1.0 cm light path quartz cells using a Varian Cary 100 UV spectrophotometer at λ_{max} of 666 nm. It was found that the supernatant from the adsorbent samples did not exhibit any absorbance at this wavelength and also the calibration curve was very reproducible and linear over the concentration range used in this study. The amount of methylene blue adsorbed was calculated from the difference between the concentrations in the solution before and after adsorption. Blanks containing no methylene blue were used for each series of experiments. The amount of methylene blue adsorbed per gram of adsorbent was calculated as the following equation:

$$q = \frac{(C_o - C_e)V}{W} \quad (1)$$

where q is methylene blue uptake ($\mathrm{mg\,g^{-1}}$), C_o is initial concentration of dye ($\mathrm{mg\,L^{-1}}$), C_e is equilibrium concentration of dye ($\mathrm{mg\,L^{-1}}$), V is the volume of solution (L), and W is the dry weight of the added adsorbent (g).

The two principal oxygenated functional groups, carboxylic and phenolic, were determined in the coal sample used in this study. Total acidity (carboxylic plus phenolic) was determined (by reaction with barium hydroxide) via the method used by Miller et al. [26]. Carboxylic groups have been determined (by reaction with calcium acetate) according to the method of Blom et al. [27]. The phenolic group concentration was then calculated by subtracting the value for the carboxylic content from the total acidity. The results are given in Table 1.

2.3. *Characterization of adsorbent*

2.3.1. *BET analysis*

The BET surface area of the coal was measured through N_2 adsorption at 77 K in the relative pressure range from 0.05 to 0.4 using Belsorp mini II Bel, Japan. The total pore volume, defined as the volume of liquid nitrogen corresponding to the adsorbed amount, was measured at a single point of $P/P^0 = 0.987$. The pore size distributions were deduced from N_2 adsorption isotherms using the Barrett–Joyner–Halenda (BJH) method [28]. Before measurements, the sample was degassed for 15 h at 100 °C in the degas port of the adsorption analyser.

2.3.2. *Fourier transform infrared (FT-IR) spectroscopy*

FT-IR spectra of lignite samples before and after adsorption of methylene blue at 293, 313 and 333 K temperatures were run on a Perkin Elmer Model 1600 FT-IR spectrophotometer using KBr pellets. Each sample was finely ground with oven-dried spectroscopic grade KBr and pressed into a disc. All samples were oven-dried at 120 °C to remove physisorbed water. Then, the spectra were recorded at a resolution between 400 and 4000 $\mathrm{cm^{-1}}$.

2.3.3. *SEM analysis*

The morphology of the lignite and methylene blue adsorbed onto lignite at different temperatures was examined by a QUANTA 400F Field Emission SEM (high resolution) at 30 kV.

2.4. *Zeta potential and conductivity measurements*

Zeta potentials of solid particles in lignite/water suspensions from the experiments at different initial pHs (3, 6, 7, 9, and 11) were measured using Zeta Meter 3.0+ (Zeta-Meter, Inc., Staunton, VA, USA) for a constant adsorption time, 60 min. The zeta potential values were corrected for temperature differences using the following equation:

$$\xi_d(\mathrm{mV}) = C_T \xi_o \qquad (2)$$

where ξ_d, C_T, ξ_o represent the corrected zeta potential value, correction factor related to temperature and the measured zeta potential value, respectively. In addition, prior to each measurement, the zeta metre was calibrated using a Min-U-Sil standard solution. Min-U-Sil is a natural type of air-floated silica produced by crushing sandstone. Its average diameter is approximately 1.1 μm. A suspension of 100 $\mathrm{mg\,L^{-1}}$ of Min-U-Sil in a 100 $\mathrm{mg\,L^{-1}}$ sodium chloride solution is easy to prepare and provides reasonably consistent results. This suspension was allowed to stand for 1 h to reach equilibrium before use. The average zeta potential of the Min-U-Sil standard solution was between −50 and −42 mV with a standard deviation of 4–6 mV.

Conductivity measurements by using a WTW LF 521 Karl Kolb conductometer (WTW Inc., Weilheim, Germany) were determined after adsorption under the same conditions as zeta potential measurements.

3. Results and discussion

3.1. *BET analysis*

In order to obtain the surface area of the coal, N_2 adsorption/desorption were carried out at 77 K and plotted as adsorbed volume versus relative pressure (Fig. 2). The obtained adsorption isotherm matches well the Type II isotherm as classified by the IUPAC [29]. This type of isotherm relates to the multi-layer physical adsorption and describes with strong interactions between adsorbate and adsorbent. The coal presents a type-H4 hysteresis loop, which can be attributed to the mesoporous structure containing open slit-shaped capillaries with wide bodies

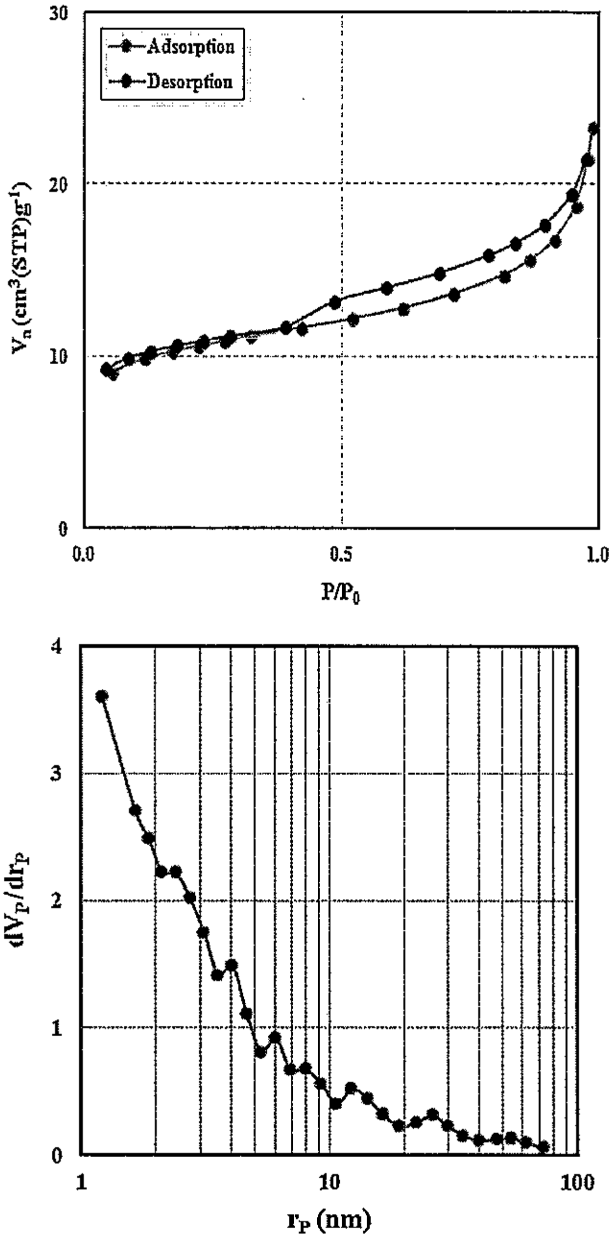

Fig. 2. N_2 isotherm of lignite and BJH plot.

and narrow short necks. Fig. 2 is the pore size distributions of the lignite sample used in this study, in which differential volume is plotted against pore size for the desorption branches of the N_2 adsorption–desorption isotherms according to BJH model. The calculated surface area and monolayer adsorption capacity of coal using the BET equation [30] was found to be 38.34 m^2/g and 8.81 cm^3/g, respectively. In addition, the total pore volume and mean pore diameter were found to be 36.14 cm^3/g and 3.77 nm, respectively. BET surface area and total pore volume of coal sample show that the lignite sample is predominantly microporous (see Fig. 2).

3.2. FT-IR spectroscopic analysis

Fig. 3 shows the FT-IR spectrum for lignite before and after adsorption of methylene blue at 293, 313 and 333 K temperatures. In the lignite sample spectrum (Fig. 3a), four regions (994–1304 cm^{-1}, 1389–1491 cm^{-1}, 1573–1692 cm^{-1}, 3421–3612 cm^{-1}) stand out due to the overlapping of several bands. The bands between 994 and 1306 cm^{-1} correspond to the angular deformation in the plane of C–H bonds of the aromatic rings (commonly appearing between 1300 and 1000 cm^{-1}), and the axial deformation of the C–O bond of carboxylic acid (commonly appearing between 1320 and 1210 cm^{-1}). The small band between 1312 and 1452 cm^{-1} was attributed to the interaction between the O–H angular deformation and the C–O axial deformation in phenols (commonly appearing between 1260 and 1180 cm^{-1}) and the C–O–H angular deformation of carboxylic acid (commonly appearing between 1440 and 1395 cm^{-1}) [31]. The bands between 1450 and 1653 cm^{-1} correspond to the aromatic skeletal vibrations involving the axial deformation of C–C bonds, which appear in the regions between 1600 and 1585 cm^{-1} and 1500 and 1400 cm^{-1}. According to Montes-Morán et al. [32], the bands observed in the region between 1700 and 1500 cm^{-1} were attributed to C–C symmetrical stretching of pyrone groups and C–O of carboxylic groups. The bands between 3421 and 3612 cm^{-1} correspond to the stretching of the O–H bond of free phenols or those that do not participate in hydrogen bonds (commonly appearing between 3700 and 3584 cm^{-1}), phenols with intermolecular hydrogen bonds (commonly appearing between 3550 and 3200 cm^{-1}), and O–H bond vibrations of carboxylic acid (commonly appearing between 3400 and 2400 cm^{-1}) [33–35]. The spectrum for methylene blue adsorbed onto lignite (Fig. 3b–d) show new bands at 1416, 1399 and 1189 cm^{-1} for dye adsorbed coal samples at 293, 313 and 333 K temperatures, respectively when compared to the spectrum of lignite surface alone. As seen from the figures the intensities of four bands belonging to both phenolic groups and carboxylic acid between 3300 and 3600 cm^{-1} change, because these groups interact with methylene blue. For this reason, the weaker bands for methylene blue adsorbed lignite samples at 1416 cm^{-1} for 293 K, at 1399 cm^{-1} for 313 K and at 1395 cm^{-1} for 333 K can be attributed to the symmetrical axial deformation of the carboxylate anion [34]. As seen from Fig. 3a, for the raw coal sample, the band in the region of 950–1120 cm^{-1} corresponding to stretching vibration of Si–O group splits into a sharp band at 1059 cm^{-1} with a shoulder around 1119 cm^{-1} attributed to perpendicular Si–O stretching [35]. The strong peak that appeared at 1030.96 cm^{-1} is indicative of the presence of siloxane (Si–O–Si) bond. For the dye adsorbed coal samples with a dye loading the shoulder at ca. 1119 cm^{-1} is markedly changed. With the methylene blue loading, the shoulder band shifted to high frequency, from 1119 cm^{-1} to 1120 cm^{-1} for adsorption at 293 K, to 1122 cm^{-1} for adsorption at 313 K and to 1126 cm^{-1} for adsorption at 333 K. After the adsorption of methylene blue, the band at the 1059 cm^{-1} shifted to 1053 cm^{-1}, to 1051 cm^{-1} and to 1047 cm^{-1} for the methylene blue adsorption at 293, 313 and 323 K, respectively. The changes in the shift and reduction of Si–O stretching band suggest that there is an interaction between the dye molecules and siloxane (Si–O) group and silicate minerals make a positive contribution to the methylene blue adsorption. According to above results, it could be said that the changing in the frequencies and intensities of bands (see Fig. 3a–d) not only relates to the interactions between methylene blue molecules and coal surface, but also relates to the increasing of dye loading as increased temperature implying the endothermic character of adsorption process.

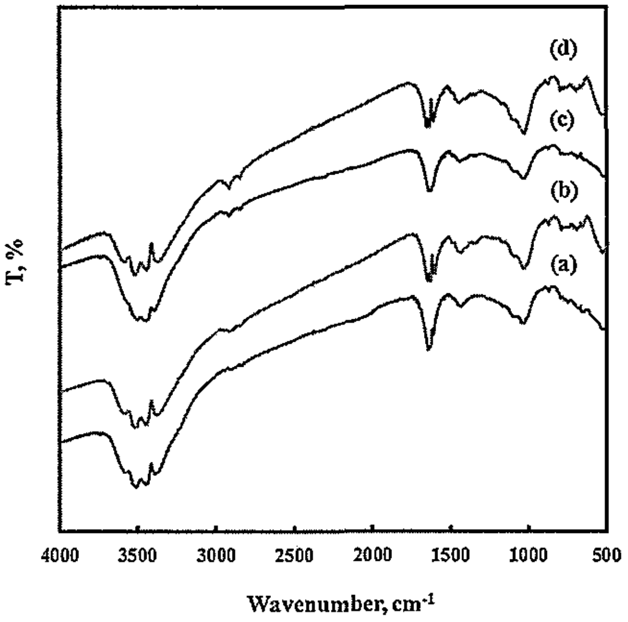

Fig. 3. The FT-IR spectrum of raw lignite (a) and after adsorption of dye at 293, 313 and 333 K (b–d, respectively).

3.3. SEM analysis

SEM analyses were performed with the purpose to confirm the adsorption of methylene blue onto lignite surface. Fig. 4a–d shows the SEM images of lignite surface before and after the adsorption of methylene blue at 293, 313 and 333 K, respectively; where the observed differences in the reflection of the images are due to the presence of methylene blue which was adsorbed. As seen from Fig. 4a, coal has a porous and rough surface and thus, there is a good possibility for dye adsorption into its pores. The contrast difference between images and the observed increase in the darkening as the temperature increased show adsorption is endothermic character.

3.4. Effect of initial dye concentration on adsorption

Effect of initial dye concentration on adsorption was investigated at different concentrations ranging from 10 to 100 mg L^{-1} of methylene blue at different temperatures. Fig. 5 shows the extent of dye adsorption as a function of reaction time and initial dye concentration at 293 K. It was found from the experimental results, 5 min is sufficient for reaching the adsorption equilibrium for 10, 20 and 40 mg L^{-1} of dye concentrations, whereas the equilibrium time for higher dye concentrations increases up to 10 min. It can be seen that an increase in the initial concentration leads to a faster uptake of methylene blue. The rate of adsorption decreases with time and gradually reaches a plateau. This may be attributed to the gradual decrease in the concentration driving force with time. It was reported that, in an aqueous solution, the absorption spectrum

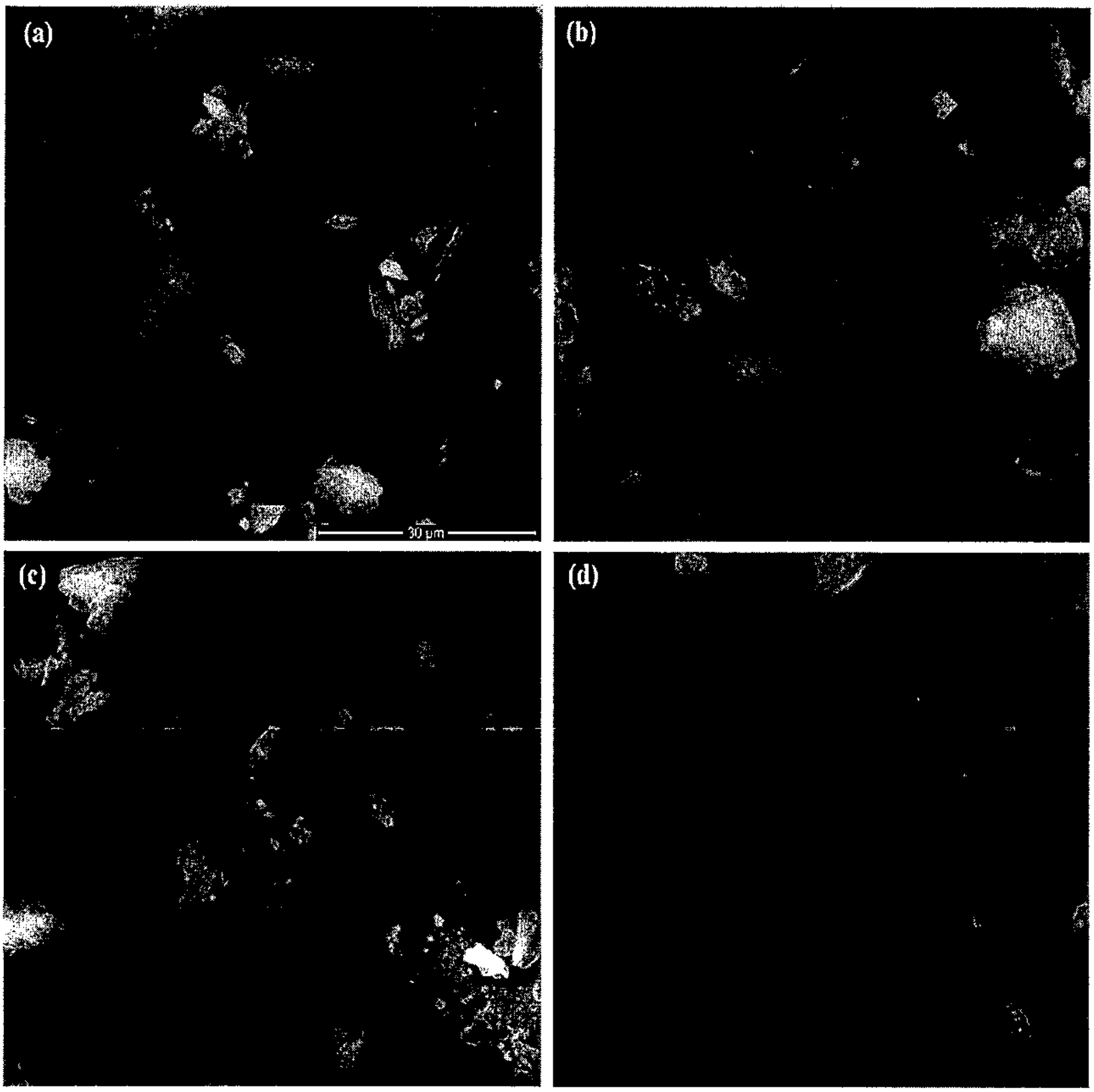

Fig. 4. SEM images of original and dye adsorbed Aşkale lignite after 60 min dye adsorption process (a) original lignite, (b) 293 K, (c) 313 K, (d) 333 K. Experimental parameters: initial dye concentration 100 mg L^{-1}, adsorbent amount 0.15 g, agitation rate 150 min^{-1}, pH natural.

of methylene blue exhibits a long-wavelength maximum at 666 nm and a short wavelength shoulder at 608 nm. The spectral shape is concentration dependent, i.e., an increase in the dye concentration causes a decrease in the monomer band (k_{max}) and a development of the more energetic band (i.e., shoulder). These features are consistent with the presence of dimeric species (H-aggregates) [36]. Also, the presence of monomer and dimer species, and their alterations in different temperature and ionic strength conditions changes the peaks of monomer and dimer [37]. In aqueous solutions and small concentration, of the order of 1×10^{-5} M, methylene blue does not show significant dimerization or aggregation [38]. Therefore, the higher equilibrium reaching time for the higher initial concentrations can be attributed to a significant dimerization or aggregation, because of the lower intraparticle diffusion rate of dimeric forms or the dimer de-aggregation and subsequent intraparticle diffusion of monomers occurring after fast initial sorption of methylene blue monomers and dimers on the external surfaces of the coal sample. Similar results were reported in previous studies [37].

3.5. *Effect of adsorbent dose*

To investigate the effect of adsorbent dose on the methylene blue adsorption onto the lignite surface, experiments were carried out with an initial dye concentration of 100 mg L^{-1} and varying adsorbent dose at 293 K and at a constant stirring speed of 150 min^{-1} for 60 min (figure not shown). The results show that the percentage removal increased with increasing adsorbent dose due to the increase in the total available surface area and the number of active sites for adsorption of the adsorbent particles. The methylene blue adsorption capacity of lignite decreases up to 0.15 g of lignite as lignite dose increases. A further increase in the

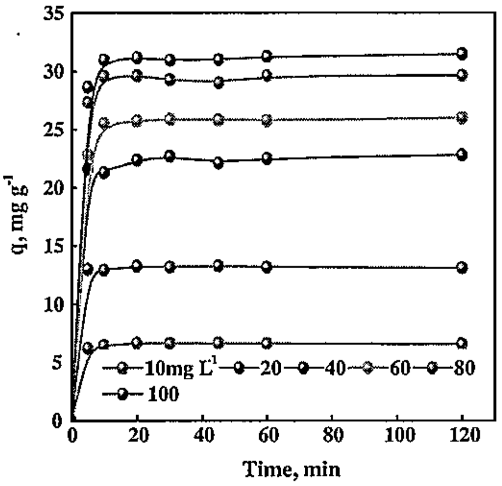

Fig. 5. Effect of initial dye concentration and contact time on the adsorption of methylene blue onto lignite. Experimental parameters: adsorbent amount 0.15 g, temperature 293 K, agitation rate 150 min^{-1}, pH natural.

adsorbent dosage did not affect the adsorbed amount of methylene blue. Therefore, an adsorbent dosage of 0.15 g was fixed for the rest of the experiments. At the same lignite dosage, higher dye concentration acquires a higher equilibrium adsorption capacity, this is because the larger dye concentration gradient increases the diffusional driving force of dye adsorbed by lignite [39].

3.6. Effect of temperature

In order to investigate the effect of equilibrium concentration on the amount of adsorbed methylene blue as a function of temperature, experiments were carried out with varying initial methylene blue concentrations (10, 20, 40, 60, 80 and 100 mg L^{-1}) at three temperatures for 10 min and at a constant stirring speed of 150 min^{-1} (Fig. 6). The observation that all of the isotherm shapes are similar to Type II and IV at all temperatures can be attributed to the heteroporous structure of the adsorbent, the strong interactions between the adsorbent and adsorbate molecules, and cooperative adsorption at higher equilibrium concentrations [40]. Both adsorption efficiency, which is the ratio of the amount adsorbed to equilibrium concentration, and adsorption effectiveness, which is the amount adsorbed at surface saturation, increased with the increasing temperature. The increase in the amount of adsorbed dye can be explained by the endothermic nature of adsorption. The temperature has two major effects on the adsorption process. Increasing temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [41]. The increasing temperature may increase the tendency of de-aggregation and so the uptake of the monomers of methylene blue. This phenomenon was also reported by other researchers [42,43]. The shapes of the adsorption isotherms serve as indicators of the orientation of the adsorbed molecules. In the present cases (see Fig. 6), the observed L-type isotherm indicates that methylene blue molecules bind strongly to lignite surface (ion-exchange-the interactions between the dye and the acidic groups of lignite) at low equilibrium concentrations, particularly at 333 K, whereas the adsorbed dye molecules prefer mutual interactions at middle and higher equilibrium concentrations.

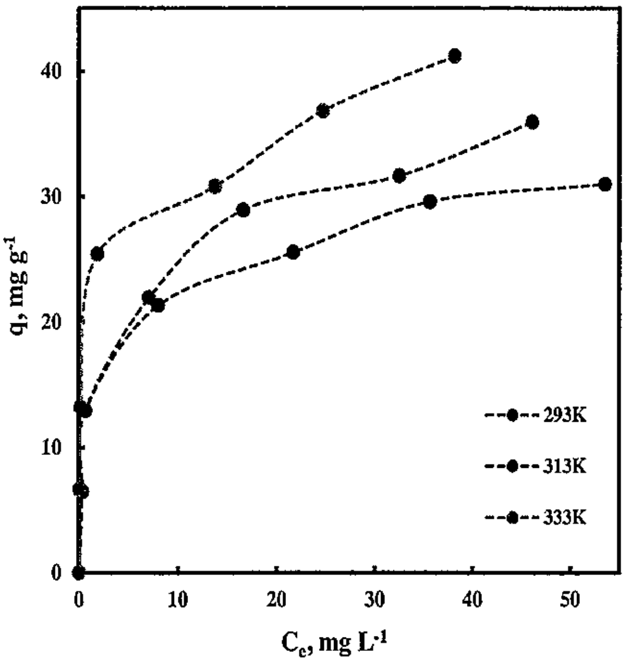

Fig. 6. The variation of the amount adsorbed (q) versus equilibrium concentration (C_{eq}) at various temperatures. Experimental parameters: adsorbent amount 0.15 g, contact time 10 min, agitation rate 150 min^{-1}, pH natural.

3.7. Effect of mixing rate

The effect of mixing rate on adsorption was investigated conducting experiments at 293 K in mixing rates 90–150 min^{-1} for 40 mg L^{-1} and 100 mg L^{-1} of initial dye concentration and at various adsorption times (figure not shown). It was seen from these experiment, mixing rate has a minor effect on the adsorption rate, indicating that the process is not diffusion controlled. Dotto et al. [44] reported that the stirring rates from 50 to 200 min^{-1} are in the average range of agitations rates for adsorption, and usually in this range a slight change in adsorption behaviour take place.

3.8. The effect of pH on the adsorption capacity, zeta potential and conductivity

The pH of dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. Fig. 7a shows the changing of adsorption capacity and zeta potential values with initial pH values (in the range of pH 3–11) of initial dye concentration of 100 mg L^{-1} for 293 K. The variation of both the zeta potentials of particles and electrical conductivity values with initial pH are also presented in Fig. 7b. As shown in Fig. 7a, the methylene blue adsorption was not clearly changed with increasing solution pH up to natural pH value (pH = 6.9). The adsorbed amounts of methylene blue slightly increased in the pH range 6.9–9.0 and then sharply increased up to pH 11. It was also seen from this figure that zeta potential values of the particles have been sharply reduced, firstly up to natural pH value, then it slightly increased and decreased with the increasing pH. After pH value of 5.5 the sign of surface charge of particles change and negative values of zeta potential decrease with increasing pH. If electrostatic interaction was the only mechanism for dye adsorption, then the removal capacity should be increased. In the pH range 4.0–8.0, mainly carboxylic group ($-CO-OH_2^+$) and, phenolic groups ($-OH_2^+$) in the lignite surface are protonated [45,46]. The constant

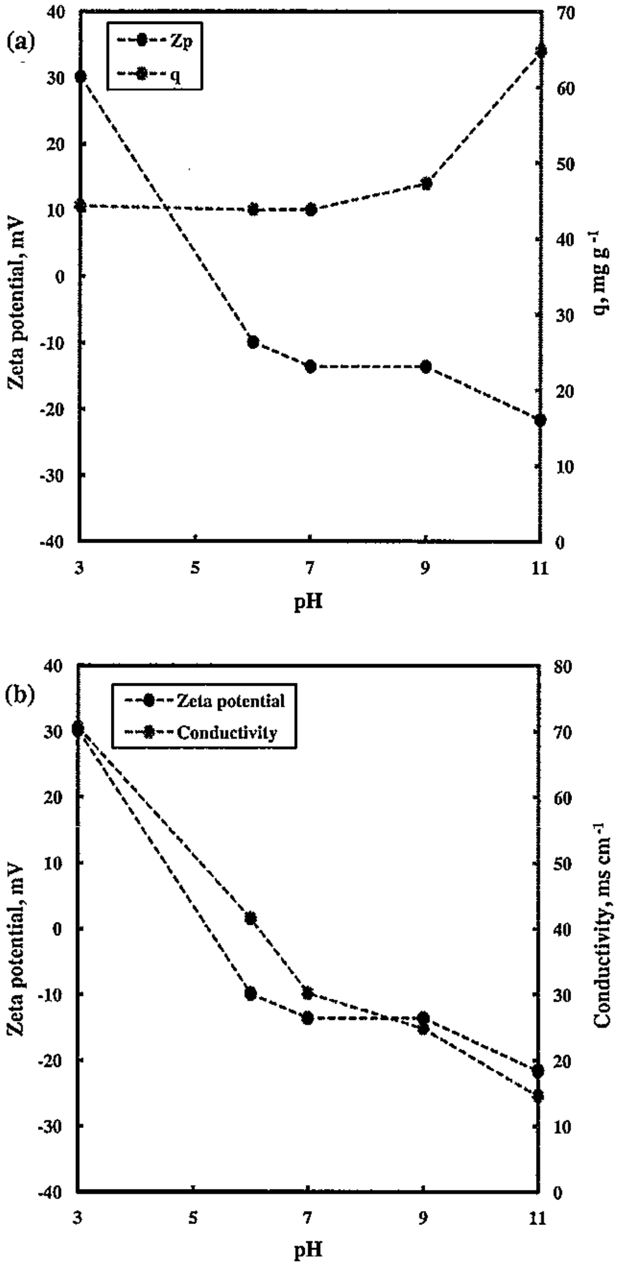

Fig. 7. The variation of both the amount adsorbed (q) and zeta potential with suspension pH (a). The variation of both the amount adsorbed (q) and electrical-conductivity values with suspension pH (b). Experimental parameters: temperature 293 K, adsorbent amount 0.15 g, contact time 60 min, initial dye concentration 100 mg L^{-1}, agitation rate 150 min^{-1}.

adsorption capacity of lignite for methylene blue in the pH range 3–7 was an indication that the electrostatic mechanism was not the only mechanism for dye adsorption in this system. Lignite sample can also interact with dye molecules via hydrogen bonding and hydrophobic bonding mechanisms [46]. The removal of methylene blue by lignite increased with changing the pH of dye solution from 7.0 to 11.0. With increasing pH values the adsorption rate of methylene blue on the lignite surface tends to increase, which can be explained by the electrostatic interaction of cationic methylene blue species with the negatively charged lignite surface. As seen from Fig. 7b, the variation in the conductivity values showed the same trend as the zeta potential change.

3.9. The effect of electrolyte

The effect of electrolyte additions on methylene blue adsorption at the lignite/water interface considering the suspension electrical conductivity, and particle zeta potential values were investigated. The experiments were carried out using the electrolytes, NaCl, $CaCl_2$ and $AlCl_3$ at different concentrations at 293 K, for 100 mg L^{-1} initial concentration of dye and for 60 min. The results are presented in Fig. 8a and b. As seen from these figures, a partial increase was occurred in the adsorbed amount of methylene blue with increasing NaCl concentration. Also, from these figures it was seen, firstly a decrease then a partial increase

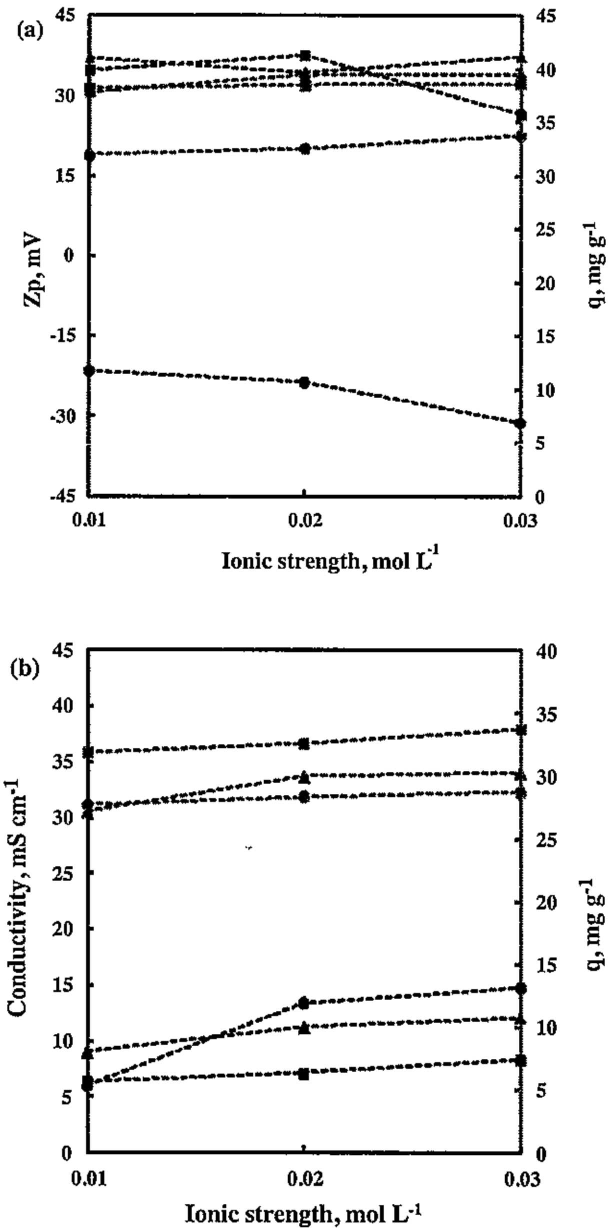

Fig. 8. The variation of both the amount adsorbed (q) and zeta potential with ionic strength (a). The variation of both the amount adsorbed (q) and suspension electrical-conductivity values with ionic strength (b). Experimental parameters: temperature 293 K, adsorbent amount 0.15 g, contact time 60 min, initial dye concentration 100 mg L^{-1}, agitation rate 150 min^{-1}, pH natural: ■ NaCl, ● $CaCl_2$, ▲ $AlCl_3$.

was observed in electrical conductivity values while firstly an increase and then a reduction in the positive values of zeta potential of particles has occurred. It is known that ions such as Na^+ are not potential determining ions. That is, the monovalent cations, such as Na^+ do not have a specific adsorption capacity. Therefore, the measured highly positive values of zeta potential of particles are a result of dye adsorption on the lignite surface. Accordingly, this situation can be attributed to the aggregation of dye molecules induced by the action of salt ions, i.e., salt ions force dye molecules to aggregate, increasing the extent of sorption on the lignite surface [42,46]. A partial decrease in electrical conductivity values and a significantly increase in the values of zeta potential for a concentration of 0.02 M NaCl supports the idea that monovalent ions promote aggregation of MB^+ ions. In the presence of $CaCl_2$, the values of electrical conductivity and the adsorbed amounts of dye increased with increasing $CaCl_2$ concentration (Fig. 8b). In the same way, the values of zeta potential of particles increased negatively, especially in the case of 0.03 M Ca^{2+} ions. Accordingly, it may be said that the hydrolysed products of $CaCl_2$ led to great deprotonation of the acidic functional groups in lignite surface and these products are able to adsorb on the lignite, especially at higher concentrations.

As shown in figures (Fig. 8a and b), the adsorbed amount of dye increased with increasing concentration of the electrolyte in the presence of $AlCl_3$ as electrolyte and also, the electrical conductivity values increased in parallel. Highly positive values of the measured zeta potential of particles do not change with increasing ion concentration. These positive values of zeta potential are a clear indication the specific adsorption of hydrolysis products of $AlCl_3$. Although a highly positive surface charge of the particles, the increase in the adsorbed amounts of dye reveals the possibility of hydrophobic binding. In addition, the increase in ionic strength in the presence of Al^{3+} ions increased the tendency of dye ions to escape from bulk solution to the surface.

3.10. Adsorption kinetics

To investigate details of the adsorption processes of methylene blue onto the lignite, we analyzed the adsorption kinetics using several models, such as the pseudo-first-order Lagergren equation, a pseudo-second-order rate equation, and the intraparticle diffusion model [47–53], which are represented by Eqs. (3)–(5), respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

$$q_t = k_i \sqrt{t} + C \tag{5}$$

where q_t is the amount ($mg\,g^{-1}$) of dye adsorbed at time t, q_e is the adsorption capacity ($mg\,g^{-1}$) at equilibrium, k_1 is the rate constant (s^{-1}) of the pseudo-first-order model, k_2 is the rate constant ($g\,mg^{-1}\,s^{-1}$) of the pseudo-second-order model, k_i is the intraparticle diffusion rate constant ($mg\,s^{-1/2}\,g^{-1}$), C is the intercept ($mg\,g^{-1}$), and t is the time (s). The experimental data for the initial concentrations of dye at three temperatures were fitted using the pseudo-first-order, pseudo-second-order kinetics, and intraparticle diffusion models. Table 2 lists the parameters obtained using each of the models. The obtained results in this study did not fit with the first-order model (Table 2). Intraparticle diffusion model did not represent the kinetics well; i.e., its regression coefficient was lower than those obtained using the pseudo second-order kinetics model (Table 2). The linearity of the plots of t/q_t versus t (linear regression coefficients: >0.990) confirmed the pseudo-second-order nature of the process. Similar phenomena have been observed for methylene blue adsorption on coir pith carbon [49], cedar sawdust and crushed brick [50], clay [3], Balkaya lignite [23] and wheat shells [51]. From the pseudo-second-order rate constant k_2 (Table 2), the activation energy E_a for adsorption of methylene blue on the lignite surface was determined using the Arrhenius equation (Eq. (6)). By plotting ln k_2 versus $1/T$, E_a was obtained from the slope of the linear plot (figure not shown):

$$\ln k = \ln A - \frac{E_a}{RT} \tag{6}$$

where E_a is activation energy ($J\,mol^{-1}$); R is the gas constant ($8.314\,J\,mol^{-1}\,K^{-1}$), T is the adsorption temperature (K). The results obtained are 49.81 kJ mol^{-1} initial dye concentration of 80 mg L^{-1}. The magnitude of activation energy gives an idea about the type of adsorption, which is mainly physical or chemical. E_a for physisorption is usually <40 kJ mol^{-1}, whereas it is higher in the

Table 2
Kinetic parameters for adsorption of methylene blue onto lignite.

Initial concentration $mg\,L^{-1}$	Temp. K	Pseudo-first-order	Pseudo-second-order				Intraparticle diffusion					
		R^2	k_2 $g\,mg^{-1}\,s^{-1}$	$q_{e,exp}$ $mg\,g^{-1}$	$q_{e,cal}$ $mg\,g^{-1}$	R^2	k_{i1} $mg\,s^{-1/2}\,g^{-1}$	C	R^2	k_{i2} $mg\,s^{-1/2}\,g^{-1}$	C	R^2
10	293	0.0056	–	6.4422	6.5876	1.0000	0.0024	5.81	0.9924	–	6.7204	0.9354
20	293	0.1373	–	12.9194	13.1406	1.0000	0.0163	13.00	0.6296	–	13.348	0.5024
40	293	0.1373	0.0015	21.3152	22.8310	0.9999	0.0520	20.45	0.7990	0.0186	21.256	0.8779
60	293	0.2183	0.0020	25.5252	26.0416	1.0000	0.1570	20.68	0.7120	0.0042	25.297	0.5526
80	293	0.1493	0.0021	29.5803	29.6735	0.9999	0.1221	25.73	0.6687	0.0116	28.685	0.4763
100	293	0.0721	0.0015	30.9641	31.4465	1.0000	0.1373	26.75	0.7223	0.0001	30.775	0.8806
10	313	0.0343	0.0166	6.6097	6.6357	0.9999	0.00006	7.00	0.0021	0.0013	6.5244	0.1317
20	313	0.0503	0.0065	12.9256	13.2978	1.0000	0.0391	11.90	0.9736	0.0110	13.179	0.1289
40	313	0.0011	0.0012	21.9412	22.9357	0.9996	–	21.97	0.7247	0.0152	21.589	0.3489
60	313	0.0390	0.0010	28.9144	29.3255	0.9996	0.1347	24.62	0.6499	0.0108	28.196	0.2674
80	313	0.1440	0.0008	31.6489	32.4675	0.9998	0.1598	26.34	0.5680	0.0190	30.729	0.6813
100	313	0.1324	0.0117	35.9095	36.6300	0.9999	0.1627	30.84	0.6954	0.0136	35.446	0.5762
10	333	0.0002	0.0415	6.6539	6.6577	1.0000	–	6.6741	0.4327	0.0025	6.4471	0.9753
20	333	0.4037	0.0084	13.2137	13.1406	0.9996	0.0004	13.131	0.0029	0.0157	11.878	0.9974
40	333	0.0558	0.0012	25.4225	26.0416	0.9999	–	26.103	0.5710	0.0171	24.662	0.7930
60	333	0.1028	0.0011	30.7986	31.4465	0.9999	0.1349	26.308	0.5638	0.0202	29.654	0.9148
80	333	0.0875	0.0001	36.8207	37.0370	0.9999	0.1527	31.837	0.6013	0.0065	36.535	0.1327
100	333	0.1672	0.0001	41.2046	41.3223	1.0000	0.0669	38.641	0.5544	0.0104	40.395	0.8496

case of chemisorption [54,55]. This claims that the uptake rate of the dye on the lignite surface could be described by a pseudo second-order rate expression based on the strong electrostatic interactions between adsorbent and dye or chemisorption but the interactions between the lignite surface and dye ions are predominantly physical and also partly hydrophobic.

3.11. Adsorption isotherms

In order to determine the mechanism of methylene blue adsorption on the lignite surface at 293, 313 and 333 K, the experimental data were applied to the Langmuir, BET, Freundlich, Temkin, Dubinin–Radukevisch, Halsey, Harkins–Jura, Smith and Henderson isotherm equations. The constant parameters of the equations for this system were calculated by regression using the linear form of the isotherm equations and SPSS 10.0 software. The results are given in Table 3, together with the isotherm equations. The Langmuir isotherm assumes that adsorption occurs on a homogeneous surface containing sites with equal energy and that are equally available for adsorption. This is valid for the complete monolayer of adsorption, on which there is no transmigration of adsorbate on the surface plane. From the correlation coefficient (R^2) values that are regarded as a measure of the goodness-of-fit of experimental data on the isotherm's model (Table 3), it was elucidated that the Langmuir equation represent the methylene blue adsorption process on the lignite surface at the different solution temperatures very well; the R^2 values were all high, indicating a very good mathematical fit. This fitting also indicates that the adsorption of dye occurs predominantly through strong interactions (electrostatic and hydrogen bonding). Conversely, from Table 3 it may be predicted that the dye adsorption on the lignite surface is an endothermic process. The monolayer adsorption capacity of dye (q_m) increased as solution temperature was increased. K values calculated from the Langmuir isotherm model, as seen from Table 3, increased with the increasing temperature. A higher value of K implies strong interactions between dye molecules on the lignite surface. The essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called the equilibrium parameter, R_L, defined by:

$$R_L = \frac{1}{(1 + KC_o)} \quad (7)$$

where K is the Langmuir constant and C_o is the initial dye concentration. The separation factor (R_L), which is an important parameter of the Langmuir isotherm, can be used to verify if the adsorption in the system studied is unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$). In the concentration range studied (10–100 mg L^{-1}), and for each of the three temperatures (293, 313 and 333 K) the values of R_L between 0.155 and 2.0 × 10^{-3} indicate favourable adsorption in the lignite/methylene blue system. The decrease in R_L with an increase in the initial concentration indicates that the adsorption is more favourable at high concentrations (see Table 4). The Freundlich isotherm is an empirical equation that can be used for heterogeneous systems with interaction between the molecules adsorbed. From Table 3, the high R^2 value was observed for 313 K, although it was low for 293 K and 333 K. The n parameter, which is known as the heterogeneity factor, can be used to indicate whether the adsorption is linear ($n = 1$), whether it is a chemical process ($n < 1$), or whether a physical process ($n > 1$) is favourable. Conversely, the values of $1/n < 1$ and $1/n > 1$ indicate a normal Langmuir isotherm and cooperative adsorption, respectively. The value of $n < 1$

Table 3
Applicability of isotherm equations to methylene blue adsorption data of Aşkale lignite/dye system at different temperatures and their constant parameters.

Isotherm	Equation	Parameters	293 K	313 K	333 K
Langmuir	$C/q = 1/kq_m + (1/q_m)C$	q_m	31.15	35.33	41.49
		k	0.5413	0.5549	4.9183
		R^2	0.9928	0.9870	0.9845
Freundlich	$\ln q = \ln k + n\ln C$	n	0.2712	0.2603	0.3303
		k	11.24	13.37	28.23
		R^2	0.9186	0.9920	0.8937
BET	$C/q(1 - C) = 1/(q_m k) + [(k - 1/q_m k)]C$	q_m	0.1552	0.2002	0.4076
		k	−58.19	−175.25	395.66
		R^2	0.9688	0.9924	0.9888
Dubinin–Radukevisch	$\ln q = K\varepsilon^2 + \ln q_{D-R}$	K	-7×10^{-9}	-5×10^{-9}	-4×10^{-9}
		q_{D-R}	0.3096	0.3273	0.5519
		R^2	0.9450	0.9757	0.9149
		E (kJ mol^{-1})	8.45	10.00	11.18
Halsey	$\ln q = (1/n)\ln k - (1/n)\ln[\ln(1/C)]$	n	1.6149	1.3947	0.5742
		k	0.1348	0.2417	2.1209
		R^2	0.804	0.8939	0.8442
Harkins–Jura	$1/q^2 = (B/A) - (1/A)\log C$	B	−0.4249	−0.5558	−1.7076
		A	0.0128	0.0138	0.0118
		R^2	0.6494	0.8102	0.7258
Smith	$q = W_b - W\ln(1 - C)$	W	0.2719	0.4035	7.5406
		W_b	0.1412	0.1442	0.1541
		R^2	0.7085	0.7677	0.7701
Henderson	$\ln[-\ln(1 - C)] = \ln k + n\ln q$	n	2.3115	3.9513	2.7147
		k	6.6558	30.069	−1.2483
		R^2	0.7916	0.9894	0.8933
Temkin	$q_e = (RT/b_T)\ln a_T + (RT/b_T)\ln C_e$	b_T	54618.90	57700.2	176.634
		a_T	1783.88	3567.40	1.03912
		R^2	0.9792	0.9709	0.9106

q, adsorption capacity of methylene blue (mg g^{-1}); q_m, monolayer adsorption capacity; C, equilibrium concentration; n, k, K, A, B, W_a and W are constant parameters for the isotherm equations.

Table 4
Effect of initial methylene blue concentration on separation factor R_L.

Dye concentration (mg L^{-1})	Separation factor (R_L)		
	293 K	313 K	333 K
10	0.1559	0.1527	0.0199
20	0.0845	0.0826	0.0100
40	0.0441	0.0431	0.0050
60	0.0298	0.0291	0.0033
80	0.0225	0.0221	0.0025
100	0.0181	0.0177	0.0020

(Table 3) and $1/n > 1$ for 313 K in the present study indicate at the higher dye concentrations, the adsorption of aggregated ions is favourable at 313 K [56,57]. Also, in the present study, the values of k (a measure of adsorbent capacity) and n (a measure of the intensity of adsorption) for the adsorption of methylene blue onto lignite surface increasing with the increasing temperature imply the endothermic character of the adsorption process. When comparing the regression coefficient values for both the Langmuir and Freundlich isotherms, it was demonstrated that the Langmuir isotherm was the most appropriate isotherm to describe the equilibrium data for dye adsorption at the three studied temperatures.

The results belonging to BET, Halsey, Harkins–Jura, Smith and Henderson adsorption models for the methylene blue adsorption onto lignite surface at different temperatures are given in Table 3, together with the isotherm equations. As seen from Table 3, the lignite sample at different temperatures fit quite well into the BET equation, while the other models presented lower R^2 values. All these equations are suitable for multilayer adsorption. In particular, the fitting of these equations can be seen in heteroporous solids [24]. Conversely, this situation may imply the probability of adsorption of aggregated ions onto the lignite surface because the probability of multilayer adsorption for this system is weak. The obtained q_m values for the Langmuir isotherm are higher than those of the BET isotherm, implying that the lignite sample is a heteroporous material exhibiting microporous properties. Nitrogen adsorption isotherms analysis results support these findings (see Fig. 2). Like the Freundlich isotherm, the Temkin isotherm considers the interactions between adsorbates, assuming that the adsorption heat of all molecules decreases linearly when the layer is covered and that the adsorption has a maximum energy distribution of uniform bond. A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants a_T and b_T (figure not shown). b_T and a_T are a constant related to the heat of adsorption and equilibrium binding constant corresponding to the maximum binding energy, respectively [53–58]. The obtained values for a_T and b_T are tabulated together with the value of the correlation coefficient in Table 3. The fit to experimental data ($R^2 = 0.9106$) in Table 3 shows that the Temkin isotherm for 333 K is less adequate to explain the adsorption of methylene blue onto the lignite surface, as compared to 293 K and 313 K temperatures. This reveals that the dye adsorptions at 293 K and 313 K are characterized by a uniform distribution of binding energies up to some maximum binding energy and the increasing of temperature probably leads to increasing of uniformity [59,60].

The Dubinin–Radushkevich model was used to determine the characteristic porosity and the apparent free energy of adsorption. Dubinin–Radushkevich (D–R) isotherm equation [57,61]:

$$\ln q_e = K\varepsilon^2 + \ln q_{D-R} \qquad (8)$$

where q_e is the amount adsorbed of dye at equilibrium concentration (mg g^{-1}); q_{D-R} is D–R maximum adsorption capacity of the dye (mg g^{-1}), K is the D–R constant (The porosity factor, $mol^2\,J^{-2}$) and ε is the Polanyi potential given below in the equation [57,58]:

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \qquad (9)$$

where C_e is the equilibrium concentration of the dye (mg L^{-1}), R is the gas constant (8.314 J K^{-1} mol^{-1}), and T is the temperature (K). The D–R constant (K) can give the valuable information about the mean energy of adsorption using Eq. (11) [57,58,61]:

$$E = (-2K)^{-1/2} \qquad (10)$$

where E is the mean adsorption energy. The results are shown in Table 3. In addition, the mean adsorption energy (E) from the D–R isotherm, defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the solid, could be used to estimate the type of adsorption. The adsorption behaviour could be predicted as the physical adsorption in the range of 1–8 kJ mol^{-1} and the chemical adsorption in more than 8 kJ mol^{-1} [57,60,61]. The E values (Table 3) are for the adsorption of dye at 293 K, 313 K and 333 K of 8.451, 10.0 and 11.18 kJ mol^{-1}, respectively. This indicates that the adsorption of dye onto the lignite surface occurs via strong interactions (electrostatic or hydrogen bonding, because the calculated E values are not greater than 8.0 kJ mol^{-1}).

The methylene blue adsorption capacities of various potential adsorbents are shown in Table 5. Although the adsorption capacity of Aşkale lignite for methylene blue was lower than that of rattan sawdust-activated carbon, activated carbon, cotton stalk, cedar sawdust, crushed brick; it was much higher than that of coir pith carbon, wheat shells, commercial activated carbon and activated carbon. According to the results obtained, Aşkale lignite could be employed as low-cost adsorbent and could be considered as an alternative to adsorbents for the removal of colour.

3.12. Adsorption thermodynamic

Thermodynamic quantities for the adsorption of methylene blue onto lignite surface have been determined by considering certain amounts of surfactant adsorbed. These are isosteric adsorption enthalpy, $(\Delta H_{ads})_q$, and isosteric adsorption entropy, $(\Delta S_{ads})_q$, which were statistically calculated using the least squares method and experimental data. These quantities were calculated using Eqs. (11) and (12) [62]. In these calculations, the amounts of dye adsorbed at different temperatures correspond to the different equilibrium adsorbate concentrations in which adsorption capacity values exhibit the tendency to be constant. The results are given in Table 6.

$$\frac{d(\ln C)}{d(1/T)} = \frac{\Delta H_{ads}}{R} \qquad (11)$$

$$\frac{d(\ln C)}{d(\ln T)} = \frac{\Delta S_{ads}}{R} \qquad (12)$$

Table 5
Comparison of the adsorption capacity for methylene blue by various adsorbents reported in literature.

Adsorbent	q, mg g^{-1}	Reference
Rattan sawdust-activated carbon	294.12	[1]
Activated carbon	160.4	[19]
Cotton stalk	147.06	[39]
Commercial activated carbon	14	[47]
Coir pith carbon	5.87	[49]
Cedar sawdust	142.36	[50]
Crushed brick	96.61	[50]
Wheat shells	16.56	[51]
Activated carbon	9.81	[52]
Aşkale lignite	41.94	This work

Table 6
Amounts adsorbed and equilibrium concentration values for the 293, 313 and 333 K temperatures and also thermodynamics quantities for lignite/dye system.

Parameters	Temperature (K)		
	293	313	333
Equilibrium concentration, C^{a} (mg L^{-1})	0.337	0.085	0.019
Adsorption capacity, q (mg g^{-1})	6.442	6.610	6.654
Isosteric adsorption enthalpy, $(\Delta H_{ads})_q$ (kJ mol^{-1})	58.19		
Isosteric adsorption entropy, $(\Delta S_{ads})_q$ (kJ mol^{-1} K^{-1})	−0.186		
Standard free energy of specific adsorption, $(\Delta G^{\circ}_{ads})_q$ (kJ mol^{-1})	−32.373	−34.518	−30.682

[a] The values in which adsorption capacity of the lignite particles is constant.

where C and T in these equations represent the equilibrium dye concentration and absolute temperature, respectively.

The change in standard free energy (ΔG°) of adsorption was calculated from the following equation:

$$\Delta G^{\circ} = -RT\ln K \tag{13}$$

where ΔG° (kJ mol^{-1})standard free energy change, K (L mol^{-1}) is the Langmuir isotherm constant, R is the gas constant (8.314 J K^{-1} mol^{-1}) and T is the temperature (K). From experimental adsorption isotherms for methylene blue adsorption onto lignite surface at different temperatures, the isosteric enthalpy of adsorption, ΔH_{ads}, can be determined using Eq. (11) and the isosteric entropy of adsorption, ΔS_{ads}, can also be determined using Eq. (12). As can be seen from Table 6, the equilibrium concentrations used in the calculation of ΔH_{ads} and ΔS_{ads} are not values corresponding to the monolayer surface cover, although in these equilibrium concentrations the values of adsorption capacity of the lignite begin to be constant. From Table 6 it can be seen that the signs of ΔH_{ads} and ΔS_{ads} for adsorption of methylene blue onto lignite surface are positive and negative, respectively. As temperature is increased, the amount of dye adsorbed is increased, implying the endothermic nature of the adsorption process. This increase also verifies the positive sign expected of $(\Delta H_{ads})_q$. The negative values of entropy change ΔS states a decreased disorder at the solid/liquid interface during dye sorption. As the temperature increases, the mobility of dye ions increases causing the ions to escape from the solid phase to the liquid phase. Therefore, the amount of dyes adsorbed will decrease, whereas the negative values of ΔG° indicated the spontaneous and feasible nature of the adsorption process at all of temperatures and the different dye concentrations. As a result, it can be said that the adsorption results obtained from lignite/aqueous dye solution system will shed light on adsorption processes in which similar adsorbents and adsorbates are used.

4. Conclusion

This study investigated the adsorption mechanism of methylene blue, which is a cationic dye, onto the lignite sample from aqueous solution as a function of ionic strength, pH, temperature, initial dye concentration and stirring speed. In addition, evaluation of the adsorption data was supported with measurements of particle zeta potential and suspension electrical conductivity. The main findings of the study could be summarized as follows:

1. The adsorption equilibrium time was found to be approximately 5–10 min, indicating that rapid adsorption occurred through physical interactions.
2. The amount of methylene blue adsorbed onto the lignite sample increased with increasing the initial methylene blue concentration, temperature and ionic strength, although it was not affected by the stirring speed.
3. The isosteric enthalpy change was calculated as 58.19 kJ mol^{-1}. The calculated entropy value (−0.186 kJ mol^{-1} K^{-1}) was negative and small.
4. The pseudo-second-order kinetic model agrees very well with the kinetics behaviour for the adsorption of methylene blue at the lignite/water interface under different temperatures.
5. Adsorption data provided the best fit with the Langmuir isotherm model for all of the temperatures, indicating monolayer sorption on a homogenous surface.
6. The obtained q_m values for the Langmuir isotherm are higher than that of BET isotherm implying that the lignite sample is a heteroporous material exhibiting microporous properties. Nitrogen adsorption–desorption isotherms analysis results support these findings.
7. FT-IR results revealed that several functional groups on the coal surface are responsible for methylene blue adsorption.
8. The observed differences in the reflection of the SEM images of lignite and methylene blue adsorbed lignite are due to the presence of dye, which was adsorbed.

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