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**ORIGINAL PAPER**

# Characterization and investigation of natural clay performance for methylene blue removal: results of the adsorption isotherm, kinetic and thermodynamic studies*

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**Abstract**

In this study, Van-Başkale (VB) clay was used for removal of Methylene Blue (MB) dye. The characterization of VB clay was carried out with the Fourier transform infrared spectra (FTIR), Brunauer-Emmett-Teller (BET), and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX) analysis. The BET surface area was measured as 11.983 $m^2 g^{-1}$. The FTIR spectra indicated the functional groups which represented the Si-H bond, N-H bond, N-O bond and Si-C stretching vibrations. The SEM-EDX analysis of VB clay showed that its composition consisted of 61.45% O, 25.70% Si, 5.89% Al, 2.82% K, 2.28% Na, 0.97% Fe, and 0.89% Ca by weight. The effects of removal, i.e. parameters pH (2-7), temperature (298-318 K), initial concentration (10-50 mg $L^{-1}$) adsorbent dosage (0.2-3.0 g $L^{-1}$), and contact time on adsorption, were investigated. The data obtained were entered into the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models, and it was demonstrated that the correlation coefficient values for the Freundlich isotherm model were higher than for the other isotherm models. The pseudo second order (PSO) kinetic model was a better choice for studying the removal of MB than the pseudo first order (PFO) and intraparticle diffusion (IPD) kinetic models. Negative Gibbs free energy values obtained from thermodynamic calculations show that adsorption occurs spontaneously. The free energy of D-R adsorption calculated using the D-R isotherm was less than 8 kJ $mol^{-1}$, indicating that the process was physical adsorption. The activation energy ($E_A$) of this process was 29.21 kJ $mol^{-1}$ which confirmed the fact that the process was physical adsorption.

**Keywords:** adsorption, clay, methylene blue, isotherm, kinetic, thermodynamic

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# INTRODUCTION

Several types of dyes are widely used in various industrial and commercial sectors, which are the primary pollution sources of aquatic systems (Ai et al. 2011). In particular, the discharge of textile industry wastewaters, which include color fibers and fabrics, into the environment poses a potential risk of more serious environmental pollution, affecting water quality, aquatic life, humans, and the ecosystem (Egbosiuba et al. 2020). In addition, synthetic dyes are toxic, carcinogenic and mutagenic, which threatens human health (Nasuha et al. 2010, Gao et al. 2016). Thus, economically viable and effective treatment before discharging dyes with wastewater remains a challenge for industries, especially from the dyeing industry. Dyes can be classified into three types according to their structures: anionic dyes (acidic and reactive), nonionic dyes, and organic cationic dyes like methylene blue (MB) (Elmourbarki et al. 2015), which are considered more toxic than anionic ones. In our work, we have chosen methylene blue as a model dye due to its harmful effects on the environment, health and its use in the textile dyeing industry (Robinson et al. 2001). Various treatment processes have been developed to protect the environment and create a possibility of reusing treated wastewater (Sellaoui et al. 2021). They differ in the application cost and treatment performance as well as the technologies involved, for example adsorption, electrolysis, flotation, chemical precipitation, ion exchange, filtration, photocatalysis, chemical oxidation, etc. (Rida et al. 2013, Singh et al. 2018, Miyah et al. 2020, Benjelloun et al. 2021, Miyah et al. 2022). Most of these technologies are very expensive, especially when applied to high--throughput effluents (Melhaoui et al. 2021). In addition, some of these processes can generate by-products that are more toxic than the original products (Thotagamuge et al. 2021). The adsorption process is one of the most widely adopted techniques for the removal of various pollutants, for example dyes and heavy metals (Ngulube et al. 2017, Youcef et al. 2019).

Different adsorbents are used for the removal of pollutants from wastewater using adsorption techniques. Most of scientific research focuses on activated carbon, which has a high pollutant adsorption capacity, but its high cost and difficulty in regeneration stimulate the search for other adsorbents (Muttil et al. 2023, Wang et al. 2023). Most research is directed toward such treatment techniques that do not consume much energy and that use low-cost natural materials, such as clays, oil shales, zeolites, and fly ash (Miyah et al. 2019, Miyah et al. 2021, Jawad et al. 2023, Praipipat et al. 2023, Velarde et al. 2023). Several studies have been reported to evaluate the potential of these materials as adsorbents for removal of dyes from aqueous media owing to their adsorptive properties, availability, non-toxicity, natural origin, and low cost (Achour et al. 2018, Achour et al. 2022, Tetteh et al. 2022). Clays constitute the major part of natural soils and are composed of complex minerals in the form of fine particles, found in sedimentary rocks composed

mainly of phyllosilicates, quartz, and silica (Morari 2021, Lagdali et al. 2023). Clays are divided into several categories, such as smectite, kaolinite, illite, chlorite, and bentonite. Clay is increasingly important because of its properties: small size of grains, sheet structure (three layers: an octahedral layer enclosed between two tetrahedral layers), the negative charge of particles on its surface, swelling, and porosity (Kausor et al. 2022). Clays invariably contain exchangeable ions on their surface and play an important role in the environment by acting as a natural scavenger of pollutants, taking up cations and/or anions either through ion exchange or adsorption or both. The prominent ions found on clay surface are $Ca^{2+}$, $Mg^{2+}$, $H^+$, $K^+$, $NH_4^+$, $Na^+$, and $SO_4^{2-}$, $Cl^-$, $PO_4^{3-}$, $NO_3^-$. These ions can be exchanged with other ions easily, without affecting the structure of clay mineral (Bhattacharyya, Gupta 2008). Natural clay minerals have been familiar to mankind since the earliest days of civilization. Because of their low cost, abundance in most continents across the world, high sorption properties and potential for ion exchange, clay materials are popular as strong adsorbents. They possess a layered structure and are considered as host materials for adsorbates and counter ions. Vermiculite clay has the largest surface area and the highest cation exchange capacity. Its current market price (about US$ 0.04-0.12 $kg^{-1}$) is about 20 times lower than that of activated carbon (Babel, Kurniawan 2003). In recent years, there has been an increasing interest in using clay minerals such as bentonite, kaolinite, diatomite and Fuller's earth owing to their capacity to adsorb not only inorganic ions but also organic molecules. In particular, interactions between MB and clay particles have been extensively studied (Gurses et al. 2004, Gucek et al. 2005, Hajjaji et al. 2006, Al-Futaisi et al. 2007, Hong et al. 2009, Kausar et al. 2018).

The clay minerals exhibit a strong affinity for MB. Relatively good removal capabilities of clays to uptake MB have been demonstrated by many researchers. The removal performances of Fuller's earth and commercial activated carbon (CAC) for MB were compared, and the results showed that the adsorption capacity of Fuller's earth is greater than that of CAC. Moreover, Fuller's earth is an interesting adsorbent since its average price is US$ 0.04 $kg^{-1}$, whereas CAC costs US$ 20 $kg^{-1}$ (Atun et al. 2003). The adsorption of MB onto diatomaceous earth (diatomite) was studied, and the results showed that this naturally occurring material could substitute activated carbon as an adsorbent due to its good availability, low cost, and good sorption properties. Further, its adsorption isotherms revealed that adsorption equilibrium was reached within 10 min (Shawabkeh, Tutunji 2003). The removal of MB from synthetic wastewater by using montmorillonite was studied, and the results indicated that it was an efficient adsorbent, for which equilibrium was attained in less than 30 min (Almeida et al. 2009). The MB removal with clay was carried out, and an adsorption capacity of 300 mg $g^{-1}$ was determined, which suggested that it is a good adsorbent for MB removal owing to its high surface area (Bagane, Guiza 2000). The adsorption of MB on clay minerals is mainly dominated by ion-exchange processes, which means that

the sorption capacity can vary strongly with pH. The feasibility of using diatomite for the removal of reactive dyes was investigated, and the results showed that the mechanism of adsorption of dye onto diatomite is physiosorption, which depends on the particle size and the presence of electrostatic interactions dependent on pH (Al-Ghouti et al. 2003). The adsorption of dyes on kaolinite was studied, and its adsorption capacity can be improved by purification and treatment with NaOH solution (Ghosh, Bhattacharyya 2002). The results of previous studies show that clay materials may be promising adsorbents in terms of environmental aspects and purification outcome.

This study focused on the performance of natural clay obtained from Van/Başkale (Turkey) in the removal of methylene Blue from aqueous solutions. The characterization of VB clay for adsorption was achieved with the help of BET, FTIR, and SEM/EDX analysis. Effects of pH, initial dye concentration, temperature and contact time parameters were evaluated on the MR adsorption. The results of isotherm and kinetic models with thermodynamic studies were confronted with experimental data.

## MATERIALS AND METHODS

### Preparation and characterization of adsorbent

The adsorption experiments were carried out with natural clay (VB) which was obtained from the province of Van/Başkale (Turkey). The sample was washed several times with distilled water to remove fines and other adhered impurities and to achieve neutralization. The sample was dried at room temperature for a week, after which it was milled and then stored in a desiccator, having been passed through 235 mesh sieves. The specific surface area, pore size distribution and pore volume of AC were measured from the $N_2$ adsorption/desorption isotherm at 77.35 K in the range of $10^{-6}$ to 1 relative pressures determined on a Tristar II 3020 analyzer (Micromeritics, USA). The Brunauer-Emmett-Teller (BET) equation was used to calculate the total surface area and average pore-diameter. The surface functional groups on AC were evaluated with FTIR (Nicolet-IS50 model Fourier Transform Infrared spectrophotometer). The surface morphologies of VB clay before and after adsorption were obtained under a Scanning Electron Microscope (SEM, Zeiss GeminiSEM 300). The samples were coated with gold for effective imaging. Also, the elemental composition of the samples was determined with Energy Dispersive X-ray spectroscopy (EDX). Methylene blue ($C_{16}H_{18}CIN_3S$), hydrochloric acid (HCl), sodium hydroxide (NaOH) and other chemicals were purchased from Sigma – Aldrich Co, and they were used without further purification.

**Adsorption experiments**

In batch experiments, which were completed in a temperature-controlled water bath (Julabo, EC-13A), the prepared adsorbent was treated with 500 mL of dye solution. The effects of the parameters: initial dye concentration (10-50 mg $L^{-1}$), pH (2-7), adsorbent dosage (0.2-3.0 g $L^{-1}$), and temperature (298-318 K) for a contact time of 240 min on the adsorption were investigated. The pH values of solutions were adjusted to working settings by adding negligible volumes of 0.1 N HCl and 0.1 N NaOH solutions with a pH meter (Selecta, pH-2005). The optimum pH was then determined as 3.0 and used throughout all adsorption experiments, which were conducted at various time intervals, initial concentrations (10-50 mg $L^{-1}$) and temperatures (298 K, 308 K and 318 K), to determine the adsorption time and the maximum removal of dye. The MB concentration in the dye solution was determined for 240 min. The suspension was centrifuged (Nüve, NF800) at 5000 rpm for 10 min, and the supernatant was analysed for the residual MB concentration with a spectrophotometer (PG Instruments, T80/T80+) at 660 nm wavelength. All experiments were performed in duplicate in the same conditions, which were 298 K, 308 K and 318 K temperatures, and the average of the resultant data was taken as the result. The unknown MB concentrations were determined with a calibration curve which was obtained by plotting absorbance and different dye concentrations. The dye adsorption capacity on the adsorbent was calculated with Eq. (1);

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

where: $V$ symbolizes solution volume (L), $C_0$ and $C_e$ represent initial and equilibrium concentration of dye (mg $L^{-1}$), and $m$ denotes adsorbent mass (g). The dye removal percentage was determined with Eq. (2);

$$\text{dye removal percentage}\,(\%) = \frac{(C_0 - C_t)}{C_0} x100 \tag{2}$$

The effects of the adsorbent amount, pH, initial dye concentration, temperature and contact time on the adsorption of MB with the clay (VB) adsorbent were determined. Ultimately, data obtained from this study were tested by fitting the isotherm, kinetic and thermodynamic relationships for MB dye removal using natural clay (VB).

**Adsorption isotherm studies**

The Freundlich, Langmuir and Dubinin-Radushkevich isotherms were used to explain the interaction of adsorbate molecules and adsorbent surface. Both models were applied for the description of the experimental data obtained at three temperatures. The Langmuir model assumes the adsorption occurs on a homogenous adsorbent surface without interactions between adsorbates on the surface, and its equation is given in Eq. (3);

$$q_e = (q_m K_L C_e)/(1 + K_L C_e) \tag{3}$$

where: $q_m$ denotes maximum adsorption capacity (mg $g^{-1}$), $K_L$ is Langmuir constant (L $g^{-1}$). $q_m$ and $K_L$ can be determined from the slope and intercept of the straight line which is obtained by plotting $C_e/q_e$ versus $C_e$ (Langmuir 1918). The dimensionless separation factor ($R_L$) can be obtained from Eq. (4);

$$R_L = \frac{1}{1+K_L Ce} \tag{4}$$

where: $R_L$ of $0 < R_L < 1$ indicates favourable adsorption. The Freundlich isotherm is an empirical model based on adsorption that occurs on a heterogeneous adsorbent surface, and its equation is given in Eq. (5);

$$q_e = K_F Ce^{1/n} \tag{5}$$

where: $K_F$ is the Freundlich constant (L $g^{-1}$), and n is an empirical coefficient. A straight line was obtained for the plot of natural logarithm of $q_e$ versus $C_e$. The slope and intercept of the line gives $n$ and $K_F$ values, respectively (Freundlich 1906).

The Dubinin-Radushkevich (D-R) isotherm model is used to explain heterogeneous adsorption with Gaussian energy distribution. This model is generally applied to distinguish the physical and chemical adsorption of ions by their average free energy (E), which is determined per molecule of adsorbate for this relationship, and this isotherm equation is given with Eq. (6):

$$ln(q_e) = ln(q_m) - K_D * \varepsilon^2 \tag{6}$$

where: $q_m$ is the saturation capacity (mg $g^{-1}$), $K_D$ is a D-R constant ($mol^2$ $kJ^{-2}$) and  is the D-R isotherm constant which is also known as the Polanyi potential. The slope and intercept of $ln(q_e)$ versus $\varepsilon^2$ plot are show $K_D$ and $ln(q_m)$ values, respectively (Emmett, Kummer 1943). The D-R isotherm constant, , is expressed with Eq. (7):

$$\varepsilon = RTln[1 + (1/Ce)] \tag{7}$$

where $R$ is the gas constant ($8.314\times10^{-3}$ kJ $mol^{-1}$ $K^{-1}$) and $T$ is temperature (K). The mean free energy, $E$ (kJ $mol^{-1}$), of the adsorption per molecule of adsorbate is obtained from $K_D$, and the equation is given with Eq. (8):

$$E = 1/\sqrt{2K_D} \tag{8}$$

The Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm results for MB adsorption on VB clay at 318 K are given in Figure 1, Figure 2 and Figure 3, respectively. Isotherm model parameters for the Langmuir, Freundlich and D-R models are given in Table 1, and comparison of MB removal capacities by various adsorbents are given in Table 2.

## Adsorption kinetic studies

The MB removal data obtained in this study were analysed by pseudo first order (PFO), pseudo second order (PSO) and intraparticle diffusion (IPD) kinetic models. Adsorption experiments were conducted with five initial

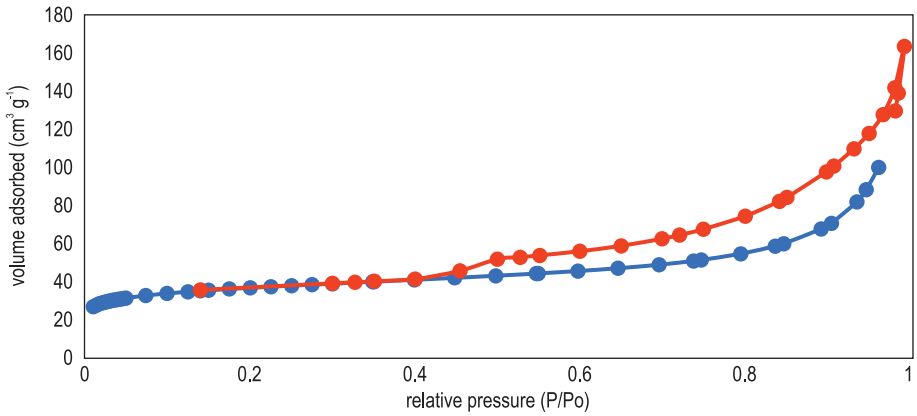


Fig. 1. $N_2$ adsorption/desorption isotherm of VB clay for adsorption

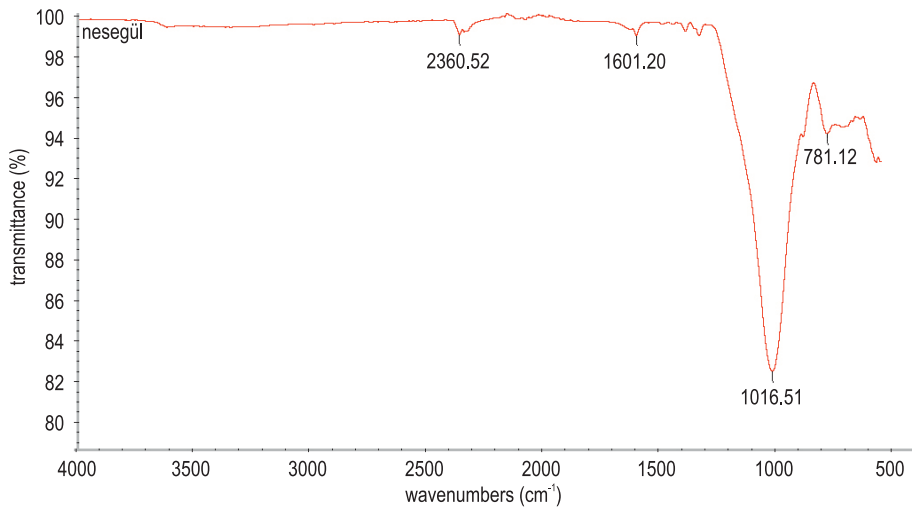


Fig. 2. FTIR spectra of VB clay for adsorption

concentrations of MB, 10, 20, 30, 40, 50 mg $L^{-1}$, respectively. The amounts of MB dye molecules adsorbed at various time periods ($q_t$) were calculated with Eq. (9);

$$q_t = \frac{(C_0 - C_t)\,V}{m} \tag{9}$$

where: $C_t$ is the concentration of MB dye molecules present in aqueous solution after $t$ min. The best-suited model was determined based on correlation coefficient ($R^2$) values. The Lagergren's equation may be the first for describing adsorption kinetics based on solid capacity and this equation is called the PFO kinetic model (Lagergren 1898). The PFO kinetic model equation is given in Eq. (10);

$$ln(q_e - q_t) = lnq_e - k_1 t \tag{10}$$

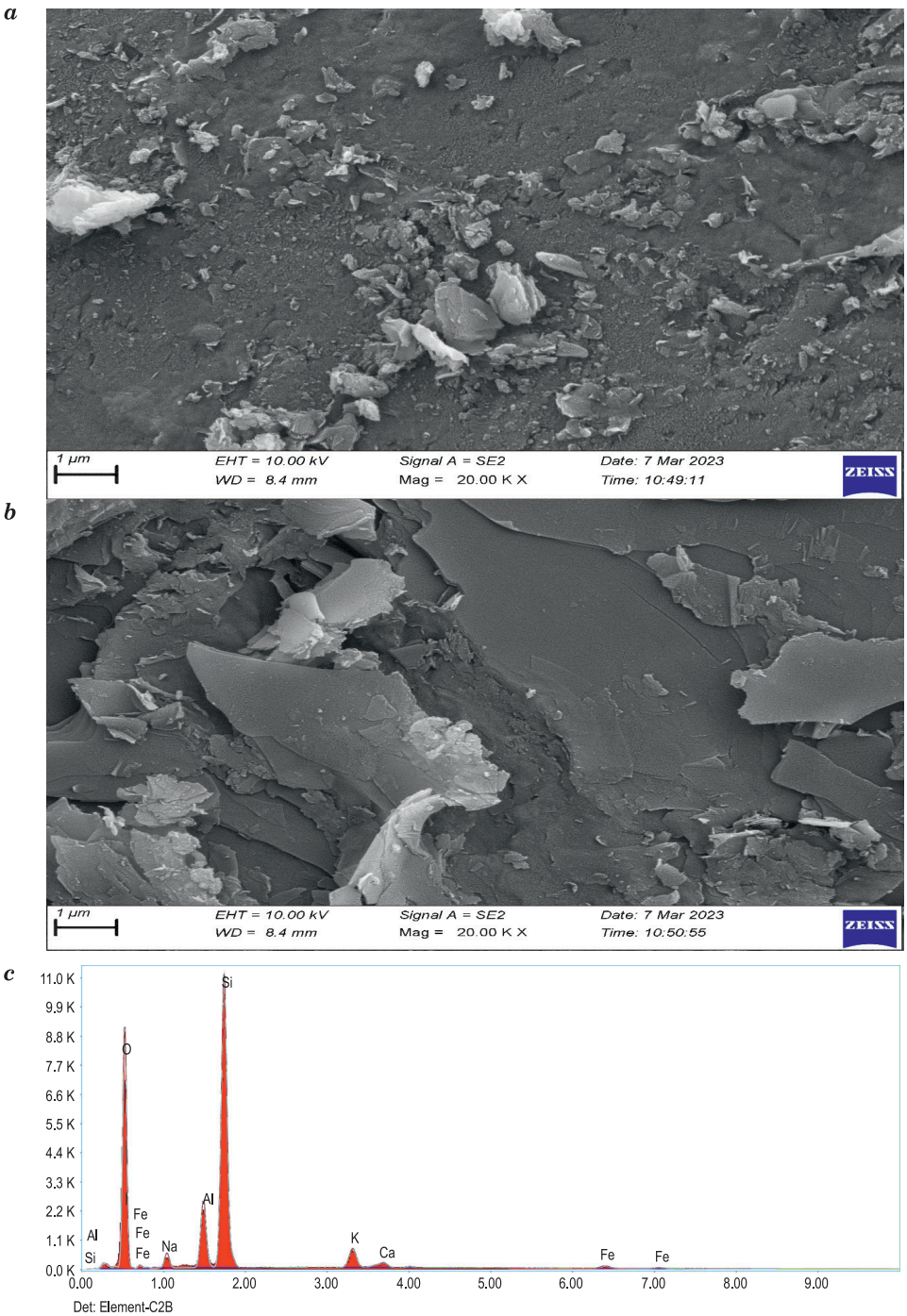


Fig. 3. SEM images of VB clay before (a), after (b) adsorption with EDX results of adsorbent (c)

Table 1

Chemical composition of VB clay

| Element | Weight (%) | Atomic (%) | NetInt | Error (%) | R | A | F |
|---|---|---|---|---|---|---|---|
| **O** | 46.46 | 61.45 | 1840.34 | 9.12 | 0.9098 | 0.2502 | 1.0000 |
| **Na** | 2.47 | 2.28 | 128.70 | 9.53 | 0.9235 | 0.4177 | 1.0066 |
| **Al** | 7.51 | 5.89 | 678.16 | 5.48 | 0.9317 | 0.6784 | 1.0177 |
| **Si** | 34.10 | 25.70 | 3080.21 | 4.41 | 0.9354 | 0.7265 | 1.0037 |
| **K** | 5.21 | 2.82 | 256.34 | 5.24 | 0.9521 | 0.8886 | 1.0166 |
| **Ca** | 1.68 | 0.89 | 69.00 | 11.21 | 0.9551 | 0.9040 | 1.0176 |
| **Fe** | 2.57 | 0.97 | 45.75 | 11.73 | 0.9728 | 0.9814 | 1.0622 |

Table 2

Isotherm model constants for MB adsorption onto VB clay

| Isotherm/Temperature | | 298 K | 308 K | 318 K |
|---|---|---|---|---|
| Langmuir | $K_L$ (L $g^{-1}$) | 0.0404 | 0.1425 | 0.1791 |
| | $q_m$ (mg $g^{-1}$) | 33.0544 | 15.5971 | 15.1502 |
| | $R^2$ | 0.7165 | 0.8570 | 0.9372 |
| Freundlich | $n$ | 1.2194 | 1.6060 | 1.6380 |
| | 1/n | 0.8201 | 0.6227 | 0.6105 |
| | $K_F$ (mg $g^{-1}$)(L $mg^{-1})^{1/n}$ | 1.4471 | 2.2425 | 2.5247 |
| | $R^2$ | 0.9947 | 0.9847 | 0.9757 |
| Dubinin-Radushkevich | $q_m$ | 7.7684 | 7.6223 | 8.1597 |
| | $E_{D-R}$ (kJ $mol^{-1}$) | 0.7058 | 0.9929 | 1.0140 |
| | $K_{D-R}$ | 1.0038 | 0.5072 | 0.4863 |
| | $R^2$ | 0.8350 | 0.8453 | 0.9073 |

where: $k_1$ ($min^{-1}$) is the rate constant of this kinetic model. In order to obtain the constants in this model, the plot of $\ln(q_e\text{-}q_t)$ against $t$ is drawn. The PSO kinetic model explains chemical bond formation between adsorbent and solute molecules based on adsorption capacity (Ho, Mc Kay 1999). The PSO kinetic model is given with Eq. (11);

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \tag{11}$$

where: $k_2$ represents the adsorption rate constant (g $mg^{-1}$ $min^{-1}$). $k_2$ and $q_e$ values were identified from the plot of $t/q_t$ versus t. IPD kinetic model was done by testing the possibility of IPD as rate limiting step using IPD kinetic model (Weber, Morris 1963) and this model is represented with Eq. (12);

$$q_t = k_{ipd} t^{0.5} + C \tag{12}$$

where: $k_{ipd}$ (mg $g^{-1}$ $min^{-0.5}$) is rate constant and $C$ is constant of boundary thickness. A plot of $q_t$ against $t^{0.5}$ at different dye concentrations gave a linear plot. PFO, PSO and IPD kinetic parameters for MB adsorption on VB clay given in Table 3 for 10 mg $L^{-1}$ initial MB concentration.

Table 3

Comparison of the MB adsorption capacity of various adsorbents

| Adsorbent type | Adsorption capacity (mg $g^{-1}$) | Reference |
|---|---|---|
| Magnetic chitosan | 60.40 | (Yuwei, Jianlong 2011) |
| Activated charcoal | 25.25 | (Iqbal, Ashiq 2007) |
| Modified zeolite | 86.96 | (Shahryari et al. 2010) |
| Rice husk | 40.58 | (Vadivelan, Kumar 2005) |
| Lignin-chitosan | 36.25 | (Albadarin et al. 2017) |
| Palm kernel fiber | 95.41 | (El-Sayed 2011) |
| Natural clay | 84.42 | this study |

## Adsorption thermodynamic studies

The Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) parameters are significant for determination of $t$ heat changes during the adsorption process between the adsorbate and adsorbent. These parameters are determined from equations shown in Eqs. (13) - (15);

$$\Delta G^{\circ} = -RTlnK_d \tag{13}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{14}$$

$$lnK_d = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \tag{15}$$

where: $K_d$ is the thermodynamic constant (L $g^{-1}$), obtained by plotting $q_e/C_e$ versus $q_e$. ΔH° and ΔS° parameters are calculated from the plot of $lnK_d$ versus $1/T$. Thermodynamic parameters are illustrated in Table 4. The activation energy ($E_A$) provides an idea about the type

Table 4

Kinetic model parameters for MB adsorption VB clay (initial MB conc.: 10 mg $L^{-1}$)

| Model / Temperature | | 298 K | 308 K | 318 K |
|---|---|---|---|---|
| $q_{e,exp}$ (mg $g^{-1}$) | | 1.955 | 2.129 | 2.458 |
| PFO Kinetic Model | $k_1$ ($min^{-1}$) | 0.043 | 0.099 | 0.070 |
| | $q_{e,cal}$ (mg $g^{-1}$) | 0.087 | 0.188 | 0.124 |
| | $R^2$ | 0.3791 | 0.9080 | 0.7999 |
| PSO Kinetic Model | $k_2$ ($min^{-1}$) | 0.8607 | 1.8062 | 1.2822 |
| | $q_{e,cal}$ (mg $g^{-1}$) | 1.960 | 2.139 | 2.464 |
| | $R^2$ | 0.9998 | 0.9999 | 0.9998 |
| Intraparticle | $k_i$ (mg $g^{-1}$ $min^{-0.5}$) | 0.1127 | 0.1245 | 0.1413 |
| Diffusion | C (mg $g^{-1}$) | 1.0167 | 1.1117 | 1.2988 |
| Kinetic Model | $R^2$ | 0.6158 | 0.6205 | 0.6057 |

of adsorption, such as physical (0–40 kJ $mol^{-1}$) or chemical adsorption (40-800 kJ $mol^{-1}$). $E_A$ values for this process are calculated from the Arrhenius equation, which is given with Eq. (16):

$$lnk_2 = lnA - \frac{E_A}{RT} \tag{16}$$

where $k_2$ is adsorption rate constant (g $mol^{-1}$ $s^{-1}$), $A$ is the Arrhenius factor (g $mol^{-1}$ $s^{-1}$), $E_A$ is activation energy (J $mol^{-1}$), $R$ is gas constant (J $mol^{-1}$ $K^{-1}$), and $T$ is adsorption temperature (K).

## RESULTS AND DISCUSSION

### Characterization of adsorbent (VB Clay)

The nitrogen adsorption/desorption isotherm of VB clay at 77.35 K was given in Figure 1, presenting type I behaviour and suggesting the simultaneous presence of mesopores. The BET analysis of VB clay gave the BET surface area of 11.9828 $m^2$ $g^{-1}$, Langmuir surface area of 6.208 $m^2$ $g^{-1}$, average pore diameter of 12.1388 nm and a cumulative pore volume of 0.018838 $cm^3$ $g^{-1}$. Figure 2 shows FTIR spectra of VB clay, which are the peaks at 2360, 1601, 1016, and 781 $cm^{-1}$, showed that it contained functional groups. The peaks at the 2360, 1601, 1016 and 781 $cm^{-1}$ represent the Si-H bond, N-H bond, N-O bond and Si-C stretching vibrations, respectively. The surface morphologies and physical properties of VB clay before and after MB adsorption were examined by SEM/EDX analysis (Figure 3). As shown in Figure 3*a*, VB clay had a rough and heterogeneous surface, whose cavities and cracks created favored MB adsorption (Figure 3*b*). The surface elemental analysis of VB clay performed by EDX analysis (Figure 3*c*) showed a composition of 61.45% O, 25.70% Si, 5.89% Al, 2.82% K, 2.28% Na, 0.97% Fe, and 0.89% Ca by weight (Table 1). The results of characterization showed that VB clay consisted of calcite, illite, kaolinite, palygorskite, colorite, dolomite, plajiyoklas, kuvarsite.

### Effect of pH

The pH of the solutions plays an important role in the adsorption process, and changes of pH affect the dissociation of functional groups on the active sites, which in turn modifies the equilibrium properties of the adsorption process as well as the reaction kinetics (Han et al. 2014). The removal of MB dye from aqueous solution through adsorption has shown that VB clay is a good adsorbent (Figure 4). It was found that the pH of the solution had a significant impact on the adsorption process, influencing both the amount of ionization of the adsorbate and the surface charge of the adsorbent. VB clay has proved to be an effective adsorbent for the removal of MB dye via adsorption from aqueous solution (Figure 4). It has been observed that

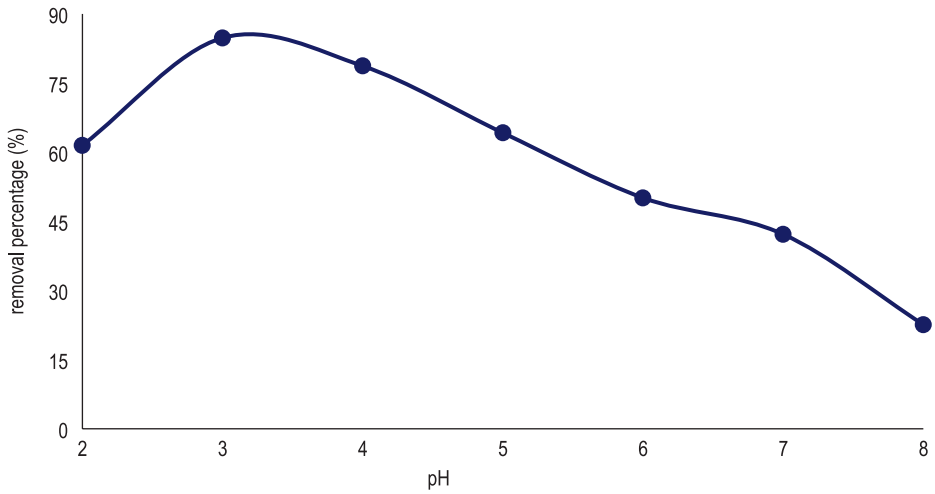


Fig. 4. The effect of pH for the MB adsorption rate on VB clay ($C_0$: 10 mg $L^{-1}$, T: 308 K)

adsorption is highly dependent on pH of the solution, in which the removal of MB decreased with increasing pH, and the optimum pH value for MB removal was found to be 3.0. The adsorption rate of MB increased from 22.60 to 84.80 mg $g^{-1}$ for VB clay, respectively, as the pH of solution decreased from 8.0 to 3.0. Similiar results of pH effects were reported for the MB adsorption on kaolin and zeolite (Rida et al. 2013).

The structural changes in the dye molecules and the surface properties of clay, which show that the capabilities of the adsorbents were pH dependent, were mostly the reason for a decrease in the removal capacity in this pH range. Natural clay surfaces have a close relationship with hydronium ($H_3O^+$) ions at low pH levels, and its surface becomes positively charged, which heightens the electrostatic attraction between positively charged adsorption sites and negatively charged dye anions, increasing the rate of adsorption. The positive charge on the oxide or solution interface has been seen to decrease as the pH of the solution gradually rises, and deprotonation of the adsorbent surface results in its negative charge, being more negatively charged sites in the solution as the pH rises (Adeyemo et al. 2017, Kausar et al. 2018).

**Effect of adsorbent dose (m)**

The study on the effect of an adsorbent dose helps to determne the maximum capacity of the adsorbent to remove MB dye. The removal percentage of MB dye by adsorption on VB clay is presented in Figure 5. Doses of the adsorbent varied from 0.2 to 3.0 g at fixed pH value (3.0) and adsorbate concentration ($C_0$: 10 mg $L^{-1}$). Figure 5 illustrates that the removal percentage of the dye had increased from 2.60 to 78.70% with an increased of the adsorbent amount from 0.2 to 0.4 g, respectively. This rapid increase in the dye

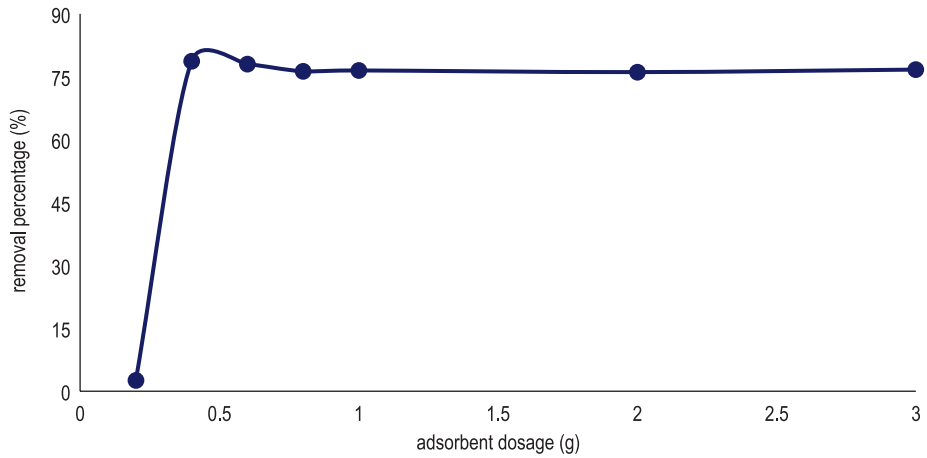


Fig. 5. Effect of adsorbent dosage for adsorption of MB on VB clay ($C_0$: 10 mg $L^{-1}$, T: 308 K)

removal with an increase in the adsorbent dose is attributed to the availability of large surface area which create more sites available for adsorption (Dogan et al. 2007, Padmavathy et al. 2016). The removal percentages decreased with an increase of the adsorbent dose above 0.4 g under constant adsorption conditions. After loading more than 0.4 g $L^{-1}$, the adsorption equilibrium is reached quickly, and therefore the odetermined optimum adsorbent dose of 0.4 g $L^{-1}$ was used in all the experiments. Similiar results on adsorbent doses were reported for MB adsorption by meranti sawdust (Ahmad et al. 2009).

**Effect of initial dye (MB) concentration**

The effect of the initial MB concentration on adsorption was investigated at concentrations ranging from 10 to 50 mg $L^{-1}$ at 298 K, 308 K and 318 K. The percentage of dye removal values decreased with an increasing initial dye concentration for the adsorbent. This result shows that increasing initial dye concentrations decrease adsorption because of the active areas on the surface of the adsorbent. Figure 6 shows that the best results for MB removal by VB clay of 84.8%, 88.9%, and 90.5% of dye were obtained at 10 mg $L^{-1}$ for 298 K, 308 K, and 318 K, respectively. The effect of initial dye concentrations for MB removal from aqueous solutions with VB clay is shown in Figure 6. These different adsorption efficiencies were due to the change in the process temperature and variation in the dye concentration. The adsorption of MB was rapid in the initial stages of contact time, when the adsorbent pores were empty, but when they filled up over time, the process slowed down, and therefore the fastest removal occurred in the first ten minutes. After saturation, the removal speed of the dye decreased slowly and then equilibrated with increasing time. As a result, adsorption equilibrium studies were performed for sixty minutes as there was not much change afterwards.

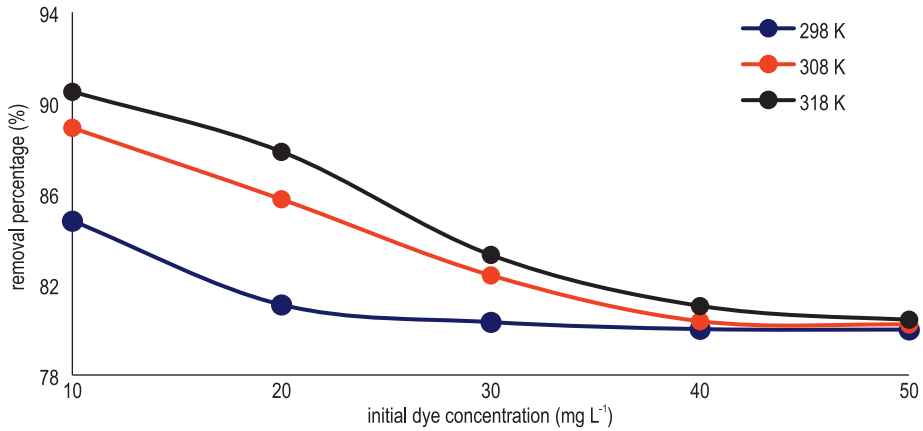


Fig. 6. Removal percentage of MB on VB clay (pH:3.0, T: 308 K)

## Effect of temperature

The effect of temperature on MB adsorption from the aqueous solutions by VB clay is shown in Figure 7. It is seen that the adsorption capability increased with increasing temperature because higher temperatures accelerate the movement of molecules. When molecules reach surface area meso-

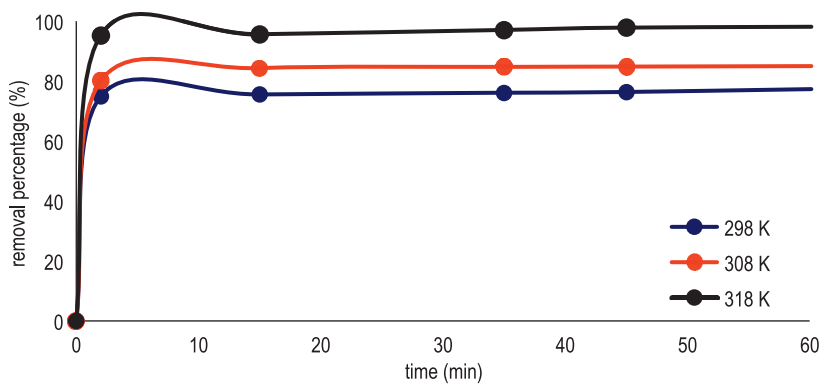


Fig. 7. Removal percentage of MB onto VB clay ($C_0$: 10 mg $L^{-1}$, pH:3.0)

pores, they can easily adhere to these pores. The 10 mg $L^{-1}$ dye concentration achieved the best removal percentage for the three temperatures tested, and the removal values of MB increased as the temperature increased for all MB concentrations. Removal percentage values increased with the temperature for each initial dye concentration (Table 3). The $R^2$ values of 10 mg $L^{-1}$ and 20 mg $L^{-1}$ initial MB concentrations which equal 1.00 were higher than those of the other concentrations. Similiar results of temperature influence were observed for MB adsorption in previous studies (Auta, Hameed 2012, Ouaddari et al. 2024).

**Isotherm results of MB adsorption onto VB clay**

The distribution of dye between the adsorbent and the dye solution at equilibrium is important in establishing the capacity of the adsorbent for dye removal from aqueous systems. The Langmuir, Freundlich and Dubinin--Radushkevich (D-R) isotherm models were chosen to explain the interaction of adsorbate molecules and the adsorbent surface in this study. All models were applied to the experimental data obtained at three temperatures. The Langmuir, Freundlich and Dubinin- Radushkevich isotherm plots of MB adsorption on clay are shown in Figure 8. The experimental data were

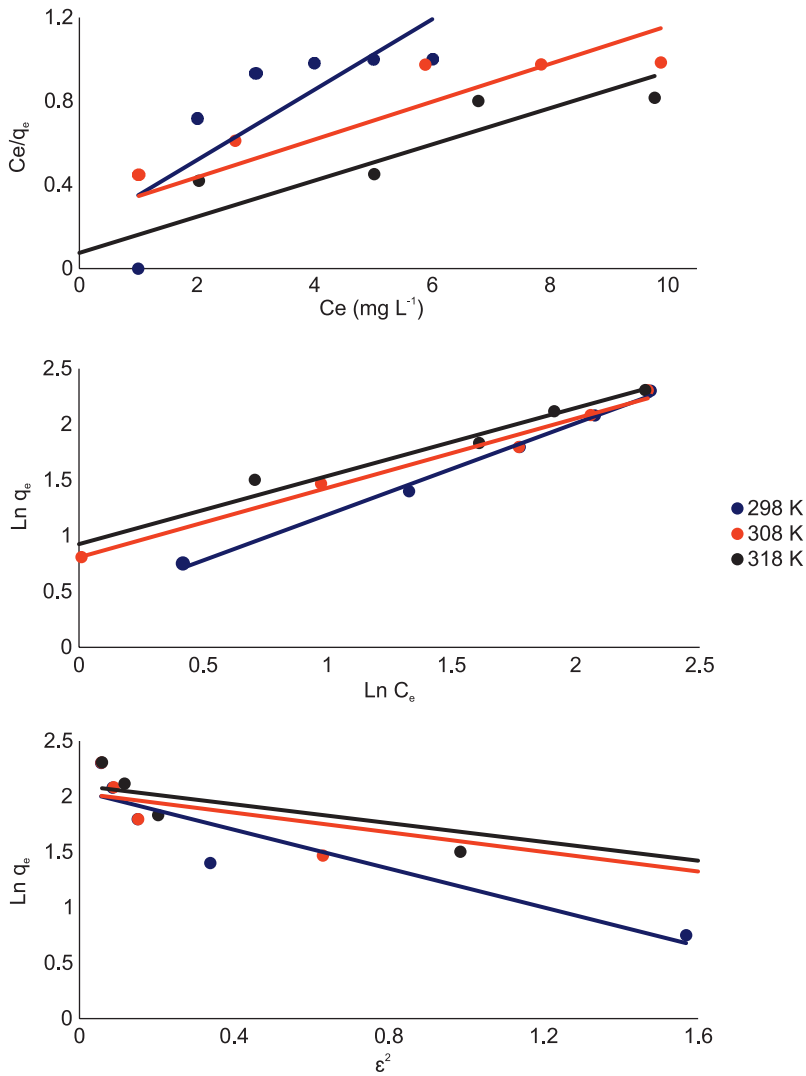


Fig. 8. Langmuir, Freundlich, Dubinin-Radushkevich isotherm plots of MB adsorption on VB clay

entered into the Freundlich, Langmuir and Temkin isotherm equations to calculate coefficients of these isotherms in order to determine the best fit of the data with the isotherm models. The coefficients of these isotherm models determined for adsorption of MB onto VB clay are presented in Table 2. $R^2$ values of the Freundlich model were higher than the Langmuir and D-R model values. With respect to the coefficients, the Freundlich model fits better than the Langmuir and D-R isotherm models, and this indicates that the adsorption of MB on VB clay takes place as multilayer adsorption on a surface that is heterogenous in terms of adsorption affinity (Ghosh, Bandyopadhyay 2017). The $K_F$ and n values increase as temperature increases, and also indicate that adsorption is more efficient at higher temperatures. Adsorption capacity ($q_m$) values were determined as 33.05, 15.59 and 15.15 mg $g^{-1}$ for 298 K, 308 K and 318 K, respectively. The adsorption intensity ($K_L$) is the Langmuir constant, which expresses the affinity of the binding sites in relation to energy. The $K_L$ values were obtained as 0.0404, 0.1425 and 0.1791 L $mg^{-1}$ for 298 K, 308 K and 318 K, respectively. The $K_L$ values increased with an increase in temperature, which accounts for the endothermic nature of the adsorption process. The separation factor ($R_L$) is used as a dimensionless constant in equilibrium concentration studies. If $R_L$ is greater than 1, it is concluded that adsorption is impeded and if the calculated $R_L$ value is between 0 and 1, adsorption is promoted. The $R_L$ values for the adsorption of MB onto VB clay are in the range of 0.331-0.101, indicating that adsorption is a favored process and that it is nearly irreversible at initial MB concentrations. The n values were determined from the Freundlich isotherm, and they show that the adsorption intensity was higher than 1.0, which indicates good adsorption by VB clay. The $K_F$ values were obtained as 1.447, 2.242 and 2.524 L $mg^{-1}$ for 298 K, 308 K and 318 K, respectively. The increase in Freundlich constants with an increase of temperature confirmed that adsorption was favored at high temperatures, and the process was endothermic in nature. The Dubinin-Radushkevich (D-R) model is generally applied to distinguish the physical and chemical adsorption of ions by their average free energy ($E$), which is determined per molecule of the adsorbate in this relationship. The calculated energy values from the D-R equation were 0.7058, 0.9929 and 1.0140 kJ $mol^{-1}$ for MB adsorption onto VB clay at 298 K, 308 K and 318 K, respectively. $E$ values were lower than 8 kJ $mol^{-1}$ for all studied temperatures, indicating that physical adsorption takes place. Various studies in the literature have investigated the use of different adsorbents for MB removal. Comparison of the adsorption capacity values of MB by various adsorbents are given in Table 3. When the results of case studies and those achieved in our experiment are compared, VB clay appears to have a relatively high adsorption capacity for MB. This suggests that MB could be easily adsorbed on VB clay, and this clay can be used as an abundant, inexpensive and effective adsorbent for MB removal from aqueous solutions. Similiar results of isotherm studies were obtained for MB adsorption by the Strychnos potatorum seeds (Senthamarai et al. 2013).

## Kinetic results of MB adsorption onto VB clay

The experimental data were applied to the PFO, PSO and IPD kinetic equations to calculate coefficients of these kinetic models in order to determine the best fit of the data obtained with a given kinetic model. PFO, PSO and IPD kinetic plots of MB adsorption on clay are shown in Figure 9. Kinetic parameters in the PFO, PSO and IPD models for MB adsorption onto VB clay are given in Table 4. The correlation coefficient ($R^2$) values of the PFO and IPD kinetic models were lower than that of the PSO kinetic model; thus, these models are not rate-limiting steps. The $R^2$ (0.99) for the PSO kinetic

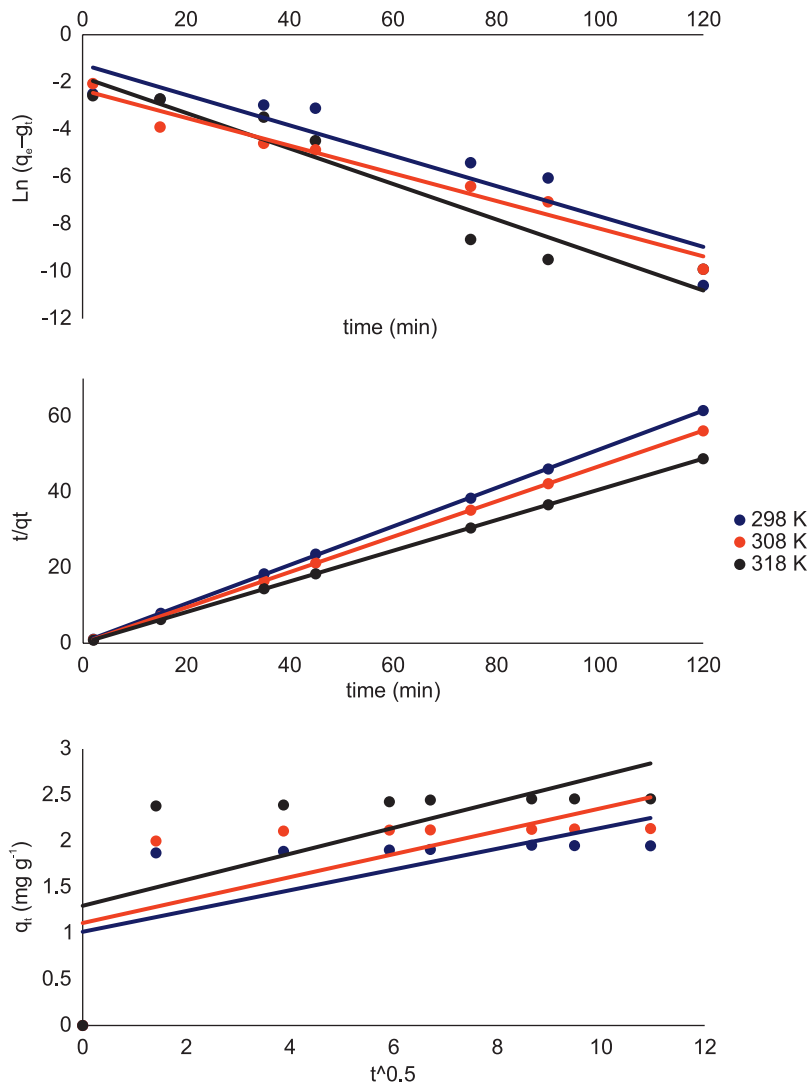


Fig. 9. Kinetic plots of the PFO, PSO and IPD models for MB adsorption on VB clay

model was close to 1.0 and indicates that the highest $R^2$ coefficients with calculated $q_e$ values for the process achieved the best fit in the PSO model. The PSO kinetic results show that the theoretical $q_e$ and the experimental $q_e$ values are relatively close compared to their distance in the other models. The adsorption process of MB on VB clay may be dominated by chemical adsorption. According to the kinetic results, it is obvious that the $q_e$ values determined according to the PFO and PSO models increased with an increasing temperature and initial dye concentration (Table 4). The kinetic results show that MB adsorption on VB clay abides by the PSO model and suggests that the rate-limiting step is explained by electron exchange between the VB clay and MB molecules. Kinetic data for adsorption are better represented by the PSO model for most dye removal processes. Similar kinetic results were observed for the MB adsorption in previous studies (Vadivelan, Kumar 2005, Albadarin et al. 2017).

## Thermodynamic results for MB adsorption onto VB clay

Thermodynamic parameters for MB adsorption onto VB clay were calculated using Eqs. (12) - (14), and the Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) values are given in Table 5. The values obtained for ΔG° and ΔH° can help in describing the mechanism of the adsorption process. ΔG° values for 10 mg $L^{-1}$ concentration of MB adsorption onto VB clay were

Table 5

Thermodynamic parameters of MB adsorption on VB clay

| Initial MB conc. (mg $L^{-1}$) | Temperature (K) | ΔG° (kJ $mol^{-1}$) | ΔH° (kJ $mol^{-1}$) | ΔS° (kJ mol $K^{-1}$) |
|---|---|---|---|---|
| 10 (mg $L^{-1}$) | 298 | -0.7690 | 10.1543 | 0.0394 |
| | 308 | -1.8487 | | |
| | 318 | -2.0057 | | |
| 20 (mg $L^{-1}$) | 298 | -0.1623 | 12.4616 | 0.0453 |
| | 308 | -1.1389 | | |
| | 318 | -1.8360 | | |
| 30 (mg $L^{-1}$) | 298 | -0.0485 | 2.7517 | 0.0099 |
| | 308 | -0.0582 | | |
| | 318 | -0.5102 | | |
| 40 (mg $L^{-1}$) | 298 | -0.0036 | 2.8815 | 0.0102 |
| | 308 | -0.0546 | | |
| | 318 | -0.4689 | | |
| 50 (mg $L^{-1}$) | 298 | -0.0004 | 0.4629 | 0.0017 |
| | 308 | -0.0334 | | |
| | 318 | -0.0641 | | |

determined as -0.769 kJ $mol^{-1}$, -1.848 kJ $mol^{-1}$, and -2.006 kJ $mol^{-1}$ for 298 K, 308 K and 318 K, respectively. ΔH° and ΔS° values for 20 mg $L^{-1}$ concentration of MB removal with VB clay were calculated as 12.4616 kJ $mol^{-1}$ and 45.301 J $mol^{-1}$ K, respectively. The ΔG° values, which varied between 0 and -30 kJ $mol^{-1}$, show the feasibility of this removal process and spontaneous nature of MB adsorption on natural clay (Table 5). The absolute values of ΔG° increase as the temperature increases, showing that this separation process is better at high temperatures. Accordingly, the increase in dye removal with increasing temperatures is due to chemical bonds, electrostatic interactions and Van der Waals forces between MB and VB clay. The positive ΔH° value shows that the removal process is endothermic, and the positive ΔS° value establishes enhanced randomness at the clay–dye interface and the affinity of clay for MB (Bouna et al. 2020). The Arrhenius plot for MB adsorption on VB clay is shown in Figure 10. From the plot,

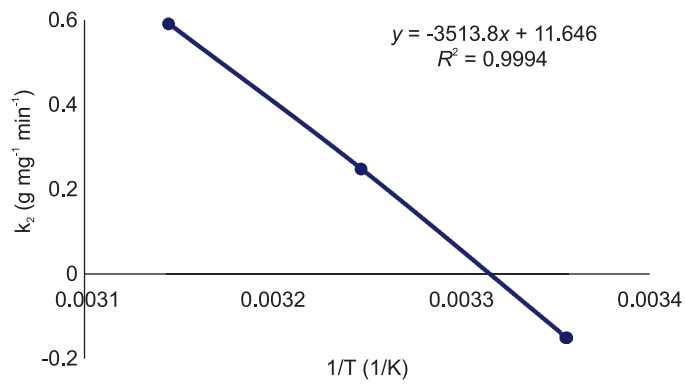


Fig. 10. Arrhenius plots for MB adsorption on VB clay

activation energy ($E_A$) was determined as 29.21 kJ $mol^{-1}$ for MB removal onto VB clay adsorbent. The activation energy was lower than 40 kJ $mol^{-1}$, which confirms the fact that the process was controlled by physical adsorption. Similar thermodynamic results were observed for the MB adsorption in previous studies (Hamed et al. 2014, Youcef et al. 2019).

## CONCLUSIONS

In this research, effects of various conditions for MB adsorption on VB clay were investigated. The characterization of VB clay was achieved with the help of BET, FTIR, and SEM/EDX analyses. The BET analysis of VB clay yielded the BET surface area of 11.9828 $m^2$ $g^{-1}$, Langmuir surface area of 6.208 $m^2$ $g^{-1}$, average pore diameter of 12.1388 nm and a cumulative pore volume of 0.018838 $cm^3$ $g^{-1}$. The FTIR spectra of VB clay indicated that it contains functional groups which represent the Si-H bond, N-H bond, N-O

bond and Si-C stretching vibrations. The elemental analysis of VB clay performed by SEM-EDX showed the composition of 61.45% O, 25.70% Si, 5.89% Al, 2.82% K, 2.28% Na, 0.97% Fe, and 0.89% Ca by weight. The results of characterization showed that VB clay consisted of calcite, illite, kaolinite, palygorskite, colorite, dolomite, plajiyoklas, kuvarsite.

The highest removal percentage of MB was achieved with the amount of 0.4 g of VB clay adsorbent. The optimum pH value for the adsorption of MB was found to be 3.0, and the removal of MB increased from 22.6 to 84.8 mg $g^{-1}$ as the pH decreased from 8.0 to 3.0, respectively. The percentages of MB removal by VB clay were obtained as 84.8%, 88.9%, and 90.5% for 10 mg $L^{-1}$ initial dye concentrations for 298 K, 308 K, and 318 K, respectively. The results showed that the removal of MB with VB clay increases with dye concentration and temperatures. When the initial dye concentration rises from 10 to 50 mg $L^{-1}$, dye adsorption capacity on VB clay decreases from 90.5 to 80.4 mg $g^{-1}$ at 318 K, respectively. Isotherm studies demonstrate that the Freundlich model shows a more suitable profile for MB adsorption on VB clay than the Langmuir and Dubinin-Radushkevich models. The parameters of these three isotherms increase as the temperature rises, which also indicates that adsorption is more favored at higher temperature. The $R^2$ values of the Freundlich model are higher than those of the other two models for MB removal with VB clay. Kinetic studies indicate that adsorption of MB follows the PSO model, suggesting that the rate-limiting step may be dye removal. The thermodynamic parameters indicate that the removal process is endothermic ,and they suggest feasibility with the spontaneous nature of adsorption on VB clay. Since the activation energy for this process was lower than 40 kJ $mol^{-1}$, it confirmed that physical adsorption was carried out between MB and VB clay. It was determined that VB clay have high adsorption performance for MB, and it could be a natural material used for removal of pollutants from wastewaters in place of costly adsorbents.

## Author contributions

N. A – conceptualization, methodology, writing – original draft, visualization, prepared figures and tables, A.R. K – methodology, resources, writing – original draft, formal analysis, validation, writing review & editing, supervision.

## Conflicts of interest

The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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