

## RESEARCH ARTICLE

### Environmental Science

# Removal of methylene blue from aqueous solution using raw laterite: an adsorption study

BM Gunathilake<sup>1</sup>, D Jayawardana<sup>1\*</sup>, PGH Pupulewatte<sup>1</sup>, S Dissanayake<sup>1</sup> and PM Manage<sup>2</sup>

<sup>1</sup>Department of Forestry and Environmental Science, Faculty of Applied Sciences, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka.

<sup>2</sup>Department of Zoology, Faculty of Applied Sciences, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka.

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**Abstract:** Existing methods for dye removal have their limitations and can be expensive and not very effective. Therefore, the search for efficient, effective, less expensive, and environmentally-friendly ways to remove industrial dyes from water remains open. Methylene blue (MB) removal from aqueous solutions is studied using raw laterite soil as a low-cost adsorbent. The physico-chemical properties and surface area were determined. Effects of parameters such as contact time, laterite dosage, pH, and ionic salts on MB adsorption by raw laterite were examined. The results showed that the maximum removal efficiency of MB adsorption was observed at pH values above 10, after 60 min of contact time, and with an adsorbent (raw Laterite) dose of 1.00 g in 100mL of dye solution. Increasing the salt concentration decreased the absorption of dye from solution. Ionic salt media containing, CaCl<sub>2</sub> and KCl have shown maximum and minimum influence, respectively, on the adsorption of MB by raw laterite soil. At the optimum conditions, the experimental adsorption capacity of raw laterite was 2.930 mg/g. The experimental data fitted the pseudo-second order kinetic model ( $R^2 = 0.99$ ). The Freundlich adsorption isotherm model ( $R^2 = 0.99$ ) showed the best fit to the experimental adsorption data. According to the Freundlich isotherm model, the calculated adsorption capacity of raw laterite was 2.949 mg/g. Desorption studies with several solvents revealed that the adsorbent could successfully retain MB, up to 33.89%. Therefore, it can be considered that raw laterite soil is effective in removing MB from aqueous solutions.

**Keywords:** Adsorbent, contamination, laterite, methylene blue.

## INTRODUCTION

The presence of dyes in industrial effluents is a significant concern due to their adverse effects on many life forms (Shooto *et al.*, 2020). Synthetic dyes have harmful characteristics such as toxicity, carcinogenicity, poor biodegradability, and a tendency to bio-accumulate (Duman *et al.*, 2018). About 15% of the total world production of dyes is lost as textile effluents, generating large volumes of coloured wastewater (Hameed *et al.*, 2007; Lassoued *et al.*, 2018). The abundant dye effluent causes aesthetic pollution, and eutrophication harms aquatic life (Houas *et al.*, 2001; Hameed *et al.*, 2007; Awomeso *et al.*, 2010). However, even after industrial wastewater treatment, the final effluent exhibits a certain degree of colour intensity, indicating further contamination (Rafatullah *et al.*, 2010). Therefore, there is a high demand for colour-free industrial effluent (Hao *et al.*, 2000).

Methylene blue (MB) is one of the most widely used dyes in the textile industry. It can cause several adverse health effects; eye burns, breathing difficulties, nausea, vomiting, diarrhoea, and gastritis can be caused by ingestion and inhalation of MB. Also, the accidental intake of large doses of MB would cause abdominal and chest pain, severe headache, profuse sweating, mental confusion, and methaemoglobinaemia (Ghosh & Bhattacharyya, 2002; Hameed *et al.*, 2007; Rafatullah *et al.*, 2010). As a result, removing MB from contaminated water is critical. Several physical, chemical, and biological methods to remove dyes from solutions, such as chemical oxidation, ozonation, membrane filtration, flotation, and adsorption, have been identified (Hao *et al.*, 2000). However, these dye removal methods have limits and are costly and ineffective. As

\* Corresponding author (daham@sci.sjp.ac.lk;  <https://orcid.org/0000-0001-9328-2729>)



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a result, seeking efficient, effective, low-cost, and environmentally acceptable technologies to remove industrial dyes from water continues.

In general, adsorption is defined as the enrichment of molecules, atoms, or ions in the vicinity of an interface (Thommes *et al.*, 2015). Adsorption is considered better in water treatment because of its convenience, ease of operation, and simplicity of design (Rafatullah *et al.*, 2010). As adsorption has broader applicability in removing different types of pollutants from water, it is extensively used in water pollution control (Pollard *et al.*, 1992). Recently, an increasing interest in utilizing clay minerals to remove dyes has been seen. Adsorption of MB with the clay minerals kaolinite and bentonite has been studied successfully (Ghosh & Bhattacharyya, 2002; Hong *et al.*, 2009; Mouni *et al.*, 2018). These studies reveal that clay minerals exhibit a strong affinity for MB, which is mainly dominated by ion-exchange processes (Rafatullah *et al.*, 2010). There have been few studies in which laterite has been utilized as an adsorbent. Laterite soil contains SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>. These ions can create both positive and negative charges on the surface at neutral pH. This makes the soil a suitable adsorbent for both cations and anions. Further, the high porosity and the availability of anion exchange sites are useful (Ranasinghe *et al.*, 2014; Mitra *et al.*, 2015). Previous studies related to laterite led to positive results in removing anions, such as fluoride (Sarkar *et al.*, 2006; Vithanage *et al.*, 2012). Further, laterite is used for the removal of phosphate (Zhang *et al.*, 2011), arsenite (Maiti *et al.*, 2013; Ranasinghe *et al.*, 2014), and metals such as copper (Pham *et al.*, 2017), lead, and chromium (Mitra *et al.*, 2015).

Laterite soil is widespread in the southwestern area of Sri Lanka, where it is known as ‘cabook’ in Sinhala. It is typically classified as a mottled earthy mass enriched in iron and aluminium hydroxides, that is somewhat dense but reasonably rapidly handled (Nayanthika *et al.*, 2018). Besides, laterite contains significant amounts of kaolinite and gibbsite, filling the cells of the kaolinite-sesquioxide matrix (Dissanayake, 1980). Raw laterite has not been investigated to remove industrial dyes from wastewater. As a result, this study aims to evaluate the optimal laterite soil parameters for MB-related sorption processes using kinetic modeling. This research aims to develop alternative dye removal systems that will not depend on chemicals to reduce the cost of wastewater treatment processes and introduce environmentally friendly, low-cost methods to treat industrial dyes.

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## MATERIALS AND METHODS

### Material selection

Laterite soil forms from metamorphic rock in Sri Lanka, containing primary and secondary minerals (Herath & Pathirana, 1983). Naturally available pristine laterite soil was collected from the southwest zone of Sri Lanka using the soil auger and air-dried to a constant mass. The air-dried samples were ground to a powder using the mortar and pestle and were mechanically sieved through a 53 µm standard sieve. Analytical grade Sigma Aldrich MB (tetramethylthionine chloride) was used as the adsorbate for batch experiments and was not purified before use in experimental studies.

### Characterization of laterite

The cation exchange capacity (CEC) of laterite soil was determined using the BaCl<sub>2</sub> Compulsive Exchange Method (Gillman & Sumpter, 1986). The pH of the laterite soil was measured using the SoilStik-2105 FieldScout pH Meter. The laterite soil's redox potentials (ORP) were measured using the WTW ProfiLine pH 3110 pH/mV meter. The conductivity of soil samples was measured using a WTW ProfiLine cond3210 conductivity meter. The loss on ignition (LOI) test was carried out to determine the organic matter (OM) and total organic carbon (TOC) contents in laterite (Wang *et al.*, 2011). The moisture content of laterite soil was measured by the direct percentage mass difference method (Nayanthika *et al.*, 2018).

$$\text{Moisture content \%} = \frac{W_{Wet} - W_{Dry}}{W_{Wet}} \times 100 \quad \dots(1)$$

where  $W_{wet}$  is the initial mass of the sample and  $W_{dry}$  is the mass of the dried sample at 105 °C until the samples reach constant weights.

The surface morphology and the structure of the laterite sample prepared were obtained with a scanning electron microscopy (SEM) using the Hitachi S-4200 field emission SEM (Zhu *et al.*, 2009). The powdered sample was analyzed for specific surface area and pore size distributions by N<sub>2</sub> adsorption at 77 K using the Autosorb IQ-MP (1 Stat.) Viton BET surface area analyzer (Gibson *et al.*, 2020). Parameters of the instrument were set according to 12.4 hours of approximate outgas time, and 300 °C final outgas temperature. Analysis was carried out for 3.25 hours using the standard analysis mode. Laterite soils were analyzed using X-Ray diffraction (XRD) using the Rigaku TTRAX III XRD instrument. The powdered samples were analyzed using Cu K-alpha radiation and wavelength 1.54 Å over 2θ ranging from 5° to 70° incremented by a step size of 0.02°, which are relevant parameters for the clay mineral observations (Zhao & Tan, 2018). FTIR (Fourier-transform infrared spectroscopy) analysis was used to identify and study the behavior of adsorption sites in laterite soil. Thus, investigations were carried out using a Nicolet iS10 spectrometer before and after adsorption, using the KBr-pellet method, and spectra were obtained in the range 4000–400 cm<sup>-1</sup> (Smidt *et al.*, 2005).

### Adsorption experiment

The stock solutions of MB were prepared by dissolving weighed dye powder to produce a concentration of 1000 mg/L. The solutions used in batch experiments were produced by diluting the stock solution to different initial concentrations. All solutions were prepared using distilled water. The adsorption studies of MB with laterite soil were carried out using a series of batch experiments using 100.0 mL solutions of 30.0 mg/L initial MB concentration. The equilibrium concentrations were analyzed using the Shimadzu UV-1900 spectrometer at the maximum wavelength of MB, 663 nm. The adsorbent dosage, contact time, effect of pH, and effect of salts on adsorption were studied to investigate the optimum conditions.

The amount of MB absorbed per unit weight of adsorbent ( $q_e$  in mg/g) was calculated as equation (2)

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad \dots(2)$$

where  $C_0$  is the initial concentration of MB dye (mg/L),  $C_e$  is the equilibrium concentration of the dye (mg/L),  $V$  is the volume of MB solution (L), and  $m$  is the dry laterite mass (g).

The percentage removal efficiency of MB from aqueous solutions was calculated using the following equation.

$$\text{Percentage removal Efficiency} = \frac{(C_0 - C_e) \times 100}{C_0} \quad \dots(3)$$

The experiments were conducted in triplicates under similar conditions.

### Adsorption kinetic studies

Kinetic adsorption experiments were conducted using a series of solutions, with an initial dye concentration of 30 mg/L, optimum equilibrium pH, and optimum adsorbent dosage at ambient temperature by varying the contact time with an agitation speed of 120 rpm. Dosages 0.5 g and 1.0 g attained equilibrium within a short period, and as it is essential to give appropriate time to analyze the equilibrium kinetics. The dosage of 0.1 g was selected for further testing since it takes 60 minutes to saturate. After completing the predetermined time interval, the solids phase was removed from the solutions by centrifugation, and MB concentrations were determined. The amount of MB adsorbed per unit mass of adsorbent ( $q_e$  in mg/g) was calculated using equation (2). Adsorption kinetic parameters can predict the rate of adsorption. This factor is essential and useful in predicting the adsorption mechanism (Divband *et al.*, 2016). The dynamics of the MB adsorption process by laterite soil were evaluated by the pseudo-first-order (equation 4; Lagergren, 1898) and pseudo-second-order (equation 5; Ho & McKay, 1999) kinetic models. The non-linear forms of these models are given below:

$$q_t = q_e (1 - e^{-k_1 t}) \quad \dots(4)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad \dots(5)$$

where  $q_t$  and  $q_e$  are the amounts of MB adsorbed on the adsorbent ( $\text{mg g}^{-1}$ ) at time  $t$  and equilibrium time, respectively;  $k_1$  is the rate constant of the pseudo-first-order kinetics ( $\text{min}^{-1}$ ), and  $k_2$  is the rate constant of the pseudo-second-order kinetics ( $\text{g mg}^{-1} \text{min}^{-1}$ ).

### Adsorption isotherm studies

Adsorption isotherm experiments were conducted using a series of solutions with initial MB concentrations of 10–50 mg/L with an optimum solution pH and optimum adsorbent at room temperature. The MB mixtures were shaken at 120 rpm and analyzed after equilibration to determine the residual MB concentration. Equilibrium data are essential requirements for the successful modeling of adsorption systems. Different theoretical and empirical relationships exist for modeling the adsorption process (Divband *et al.*, 2016). In this study, Langmuir, Freundlich, and Temkin models were applied to describe the adsorption process, and the equations are given below (Freundlich, 1909; Langmuir, 1916; Kinniburgh, 1986). The best-fit isotherm can be chosen using linear regression analysis of these models and comparing their correction coefficient ( $R^2$ ).

A linear form of the Langmuir isotherm is expressed as follows:

$$\frac{1}{q_e} = \frac{1}{q_{max} \times b C_e} + \frac{1}{q_{max}} \quad \dots(6)$$

where  $C_e$  = the equilibrium concentration of adsorbate ( $\text{mg/L}$ ),  $q_e$  = the amount of solute adsorbed per gram of the adsorbent at equilibrium ( $\text{mg/g}$ ),  $q_{max}$  = maximum monolayer coverage capacity ( $\text{mg/g}$ ),  $b$  = adsorption equilibrium constant ( $\text{L/mg}$ ).

A linear form of the Freundlich isotherm is expressed as follows:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad \dots(7)$$

Constants  $K$  and  $n$  indicate the adsorption capacity and adsorption intensity, respectively.

A linear form of the Temkin isotherm is expressed as follows:

$$q_e = B \ln K_t + B \ln C_e \quad \dots(8)$$

where  $B = (RT/b)$ .  $T$  is the absolute temperature in  $K$ , and  $R$  is the universal gas constant in ( $\text{J/mol-K}$ ). In this model,  $K_t$  is the binding constant which represents the maximum binding energy, and the constant  $B$  is related to the heat of adsorption.

### Desorption study

The laterite samples were loaded with 100 mL of 30 mg/L methylene blue dye solution, and the mixture was shaken for 60 min at 120 rpm at room temperature. The MB-loaded laterite samples were separated from the mixture by centrifuging at 4000 rpm for 10 min. The collected samples for the experiment were washed with distilled water and oven-dried at 50 °C for 24 hours and later used for desorption studies. This laterite powder was dispersed in 100 mL solutions of dichloromethane (DCM) and 9:1 DCM : methanol solutions, which contained 1 g of MB dye-loaded laterite powder. The mixtures were stirred at 120 rpm at room temperature for 60 min. Laterite was separated from the mixture by centrifuging at 4000 rpm for 10 min. The MB dye desorption capacity ( $q_{e, \text{desorption}}$ ,  $\text{mg/g}$ ) was calculated using equation (9),

$$q_{e, \text{desorption}} = \frac{V C_f}{M} \quad \dots(9)$$

where,  $q_{e, \text{desorption}}$  is the amount of dye desorbed from the dye saturated sorbent per gram of sorbent, at equilibrium ( $\text{mg/g}$ ),  $C_f$  is the MB dye concentration in the desorbing solution ( $\text{mg/L}$ ),  $V$  is the eluent solution volume ( $L$ ), and  $M$  is the dye saturated laterite weight ( $g$ ).

The desorption efficiency (%) of MB dye was calculated using equation (10),

$$D\% = \frac{q_{e, \text{desorption}}}{q_{e, \text{adsorption}}} \times 100 \quad \dots(10)$$

where,  $D\%$  is MB dye desorption efficiency (%) and  $q_{e, \text{desorption}}$ , and  $q_{e, \text{sorption}}$  are the MB dye desorption and sorption capacities (mg/g), respectively. All the experiments were performed in replicate.

## RESULTS AND DISCUSSION

### Characterization of laterite

The XRD analyses showed the presence of goethite, gibbsite, quartz, kaolinite, and haematite as significant constituents of laterite (Figure 1). Studies by Nayanthika *et al.* (2018) and Dissanayake (1980) have obtained similar results. According to the BET analysis results, the specific surface area of laterite soil was  $72.52 \text{ m}^2 \text{ g}^{-1}$  (Table 1). This is considerably higher than previous studies related to laterite soil (Vithanage *et al.*, 2012). According to the IUPAC classification, the isotherms (Figure 2) obtained are Type IV (Thommes *et al.*, 2015).

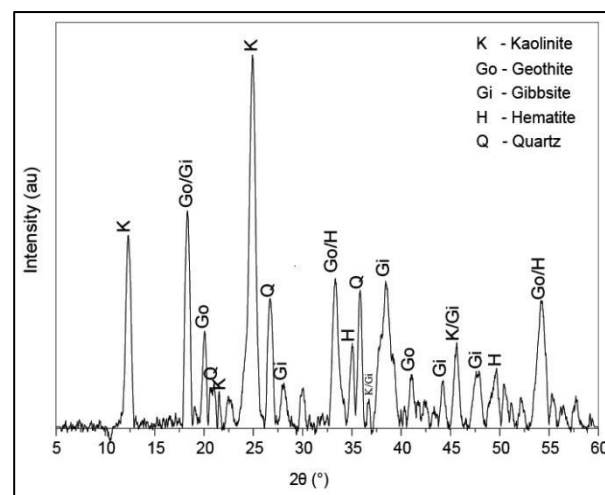


Figure 1: XRD study of raw laterite

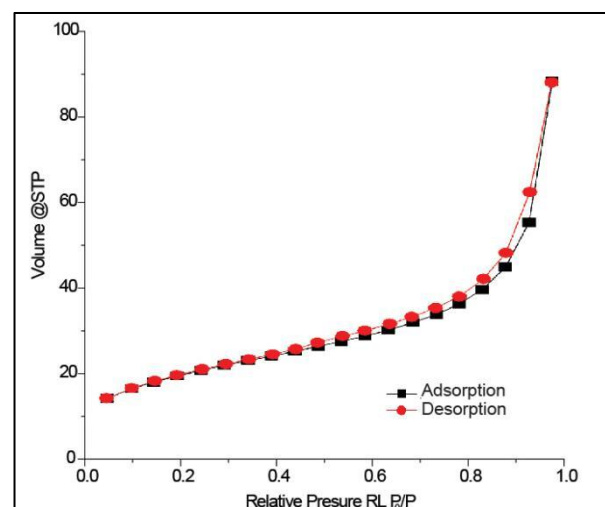


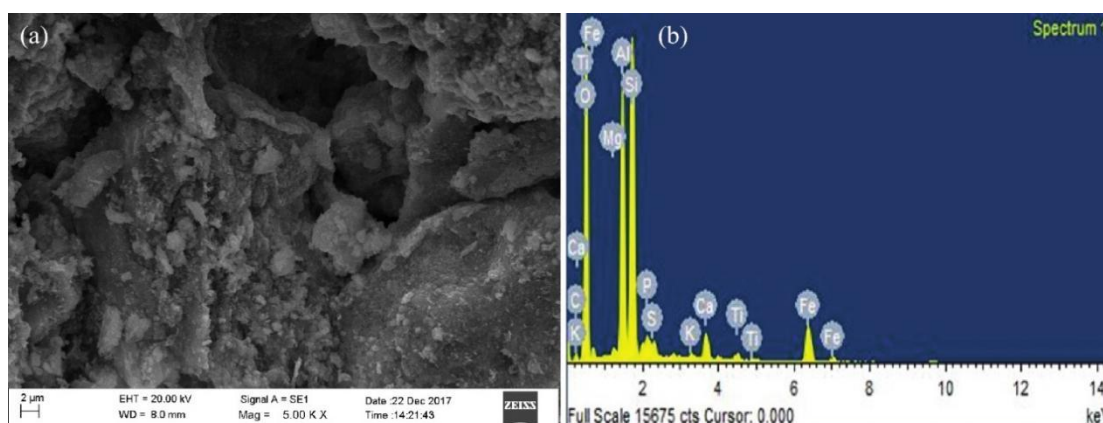
Figure 2: Low temperature nitrogen adsorption and desorption isotherms for raw laterite

Mesoporous adsorbents give Type IV isotherms. The recorded average pore radius of laterite was 3.81 nm, confirming the mesopore pore size. Mesoporous materials typically favour adsorbents due to their narrow pore size distributions, high surface area, simple functionalization strategies with organics, biocompatibility, and low toxicity (Wu & Zhao, 2011). Therefore, it confirms the applicability of laterite soil for the study.

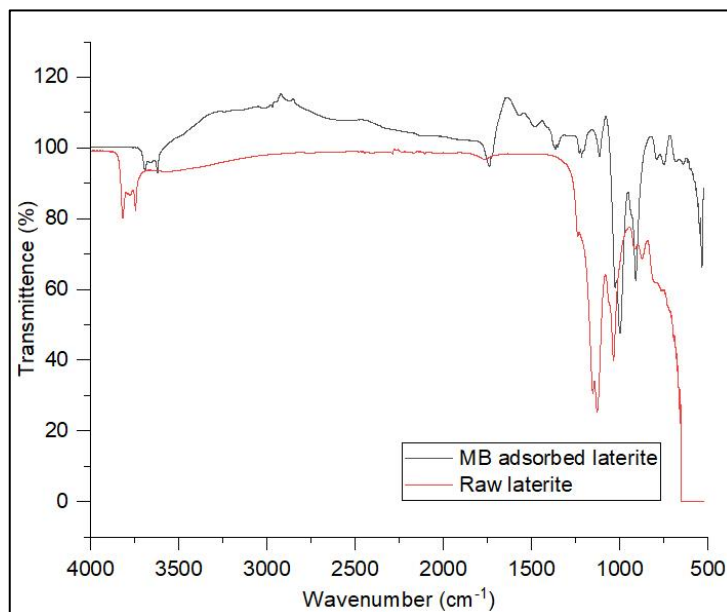
The cation exchange capacity (CEC) for the soil sample was obtained as 9.22 cmol(+)/kg (Table 1). Cationic dyes such as MB are absorbed by clay minerals mainly by cation exchange. Therefore, MB adsorption depends on exchangeable cations of laterite soil (Kahr & Madsen, 1995). The irregular and porous surface of raw laterite could be observed in the SEM images of raw laterite shown in Figure 3(a). The EDX analysis shown in Figure 3(b) further investigated the laterite soil surface. EDX results demonstrate that elements such as Fe (6.4%), Al (12.1%), Si (14.7%), O (66.2%), and Ca (1.71%) are present in raw laterite samples. The results are analogous to previous studies by Vithanage *et al.* (2012).

**Table 1:** Physico-chemical properties of raw laterite

Parameter	Values
Moisture content (%)	18.9
pH	4.7
ORP (mV)	88
EC (us/cm)	34.2
TOC (%)	7.8
OM (%)	0.74
LOI (%)	15.23
BET specific surface area (m <sup>2</sup> /g)	72.52
Average pore diameter (nm)	3.81
pH <sub>ZPC</sub>	6.6
CEC (cmol(+)/kg)	9.22



**Figure 3:** (a) SEM; (b) SEM-EDX spectra of raw laterite



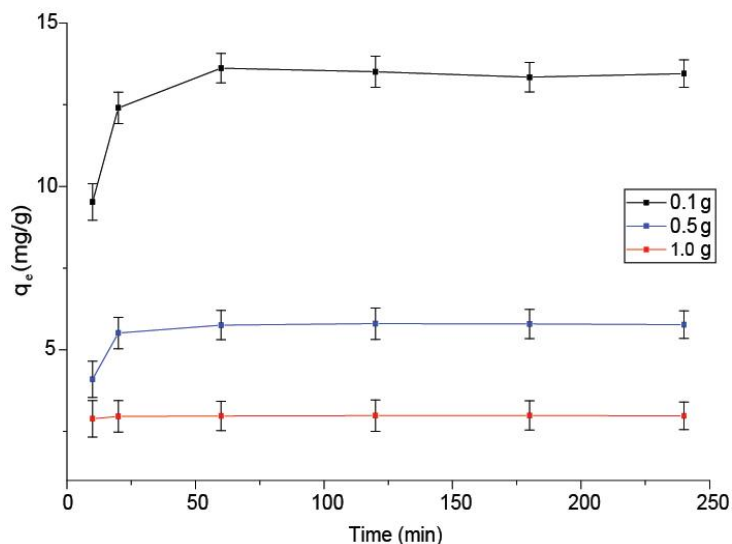
**Figure 4:** FTIR spectra of laterite before and after MB adsorption

The FTIR spectra indicate six absorption bands in the OH stretching vibration region (Figure 4) at 3818, 3799, 3792, 3779, 3773, and 3745  $\text{cm}^{-1}$  (Vithanage *et al.*, 2012). These correspond to the OH stretching vibrations of the surface and inner Al-OH groups of the gibbsite. In the region of 1200–900  $\text{cm}^{-1}$ , the bands in the region observed are 1154, 1128, 1036, and 913  $\text{cm}^{-1}$ . These can be attributed to the stretching vibrations of the Si-O-Si of free quartz and kaolinite in laterite kaolinite (Mouni *et al.*, 2018). The FTIR spectra of laterite soil after MB adsorption showed considerable changes. The broadening of the OH stretch features around 3500  $\text{cm}^{-1}$  indicates increased hydrogen bonding. Most of the IR bands that correspond to metal-oxygen bonds (M-O) and metal hydroxide bonds (M-OH), show small wavenumber shifts after MB adsorption (Vithanage *et al.*, 2012). New absorption bands were observed at 1738, 1478, 1365, 1230, and 1216  $\text{cm}^{-1}$  after MB dye was adsorbed. These bands could be assigned to -C-N-, -C=N-, and -C=C- stretching in heterocyclic poly rings of MB (Sakin Omer *et al.*, 2018). Thus, it was evident that MB adsorption had occurred onto the surface of laterite soil.

The  $\text{pH}_{\text{zpc}}$  of laterite, according to previous studies, has been calculated as 3.98 (Sarkar *et al.*, 2006), 7.40 (Pham *et al.*, 2017) and 8.72 (Vithanage *et al.*, 2012). The  $\text{pH}_{\text{zpc}}$  varies with the composition of the laterite sample (Zhang *et al.*, 2016). In this study, it was found to be 6.60.

### Effect of contact time

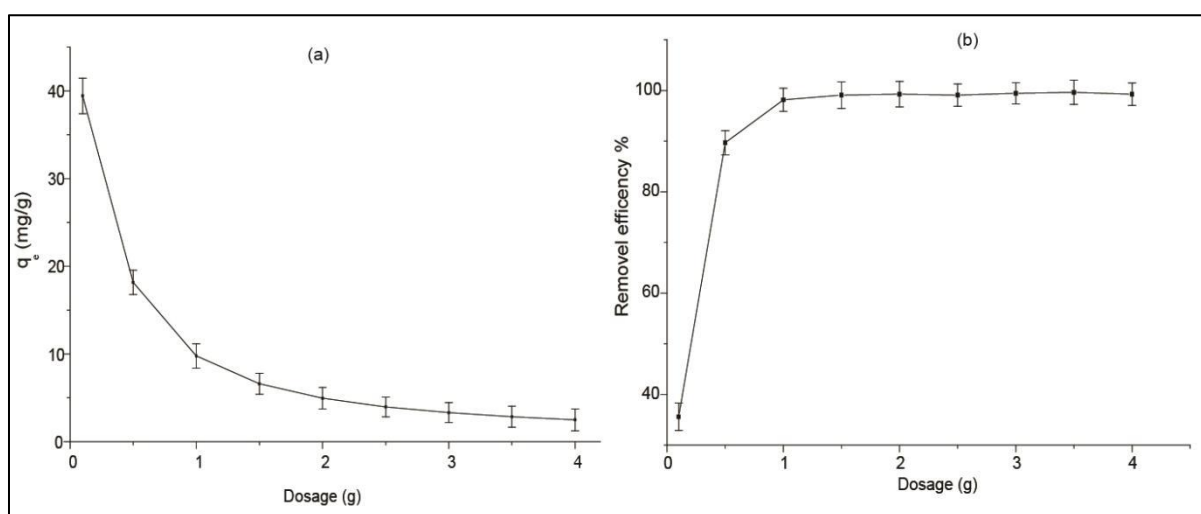
The effect of contact time on the MB adsorption capacity of laterite soil was determined with the initial MB concentration of 30 mg/L at different adsorbent dosages, from 0.1 g to 1.0 g per 100 mL of MB solution. (Figure 5). It was found that the MB adsorption capacity of laterite was rapid at the beginning stages of contact time. After 20 minutes, the adsorption rate decreases with time, and the adsorption process reaches equilibrium within 60 minutes. This process might be due to a higher number of binding sites and free pores available on laterite for the adsorption of MB during the initial stages. However, the free binding sites and pores were used as time passed, and the rate slowed down due to binding sites and pores getting exhausted. After this point, adsorption was controlled only by the rate at which MB molecules were transported from the exterior to the interior sites of the adsorbent (Shooto *et al.*, 2020). Similar results were also reported by other researchers where the MB adsorption was found to increase with the increase in contact time, but after reaching equilibrium, adsorption remained constant (Hameed & Ahmad, 2009; Mouni *et al.*, 2018; Shooto *et al.*, 2020). Therefore, according to the obtained results, a contact time of 60 minutes was chosen for further experiments.



**Figure 5:** Effect of contact time on the MB removal efficiency of raw laterite,  $C_0 = 30$  mg/L, Volume of MB solution = 100 mL

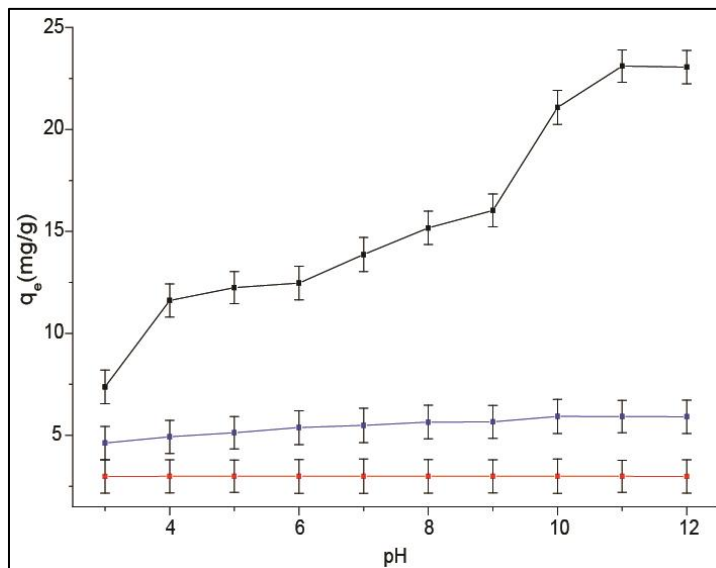
### Effect of dosage

Adsorbent dosage is another important factor in determining the optimum adsorbent dose required to remove a definite amount of pollutants from the solution. In general, an increase in adsorbent dosage increases the adsorption of adsorbate from the solution due to the availability of more active sites and increases in surface area at higher dosages (Divband *et al.*, 2016). It was evident that with the increase in adsorbent dosage from 0.1 to 4.0 g, the MB adsorption capacity decreased (Figure 6a), and the removal efficiency of laterite increased (Figure 6b). This could be related to the use of the surface area in an unsaturated form. According to the findings of this study, increasing the laterite dosage from 0.5 to 4.0 g reduced the  $q_e$  (mg/g) from 39.40 to 2.49 mg/g (Figure 6). This means that, while an adsorbent's mass increase can give a large accessible surface area, the pollutant's unsaturated adsorption pattern causes the adsorbent to be used in an undesirable way (Ong *et al.*, 2007). This concept is particularly relevant in the development of cost-effective and large-scale industrial dye removal systems.



**Figure 6:** (a) Effect of adsorbent dosage on MB adsorption capacity ( $q_e$ ) of raw laterite in 100 mL of MB; (b) effect of adsorbent dosage on the MB removal efficiency of raw laterite,  $C_0 = 30$  mg/L,  $t = 60$  min, Volume of MB solution = 100 mL

Further increase in adsorbent dosage beyond 1.0 g did not significantly affect the MB removal efficiency. Similar results were reported by other researchers where MB removal efficiency from aqueous solutions increased up to the optimum dosage, and with further increase in adsorbent dose, the removal efficiency remained constant (Franca *et al.*, 2009; Mouni *et al.*, 2018). Therefore, based on the results of this study, an adsorbent dosage of 1.0 g was selected for further experiments.



**Figure 7:** Effect of pH on MB adsorption on the raw laterite at 25 °C,  $C_0 = 30$  mg/L,  $m = 1.0$  g,  $t = 60$  min, Volume of MB solution = 100 mL

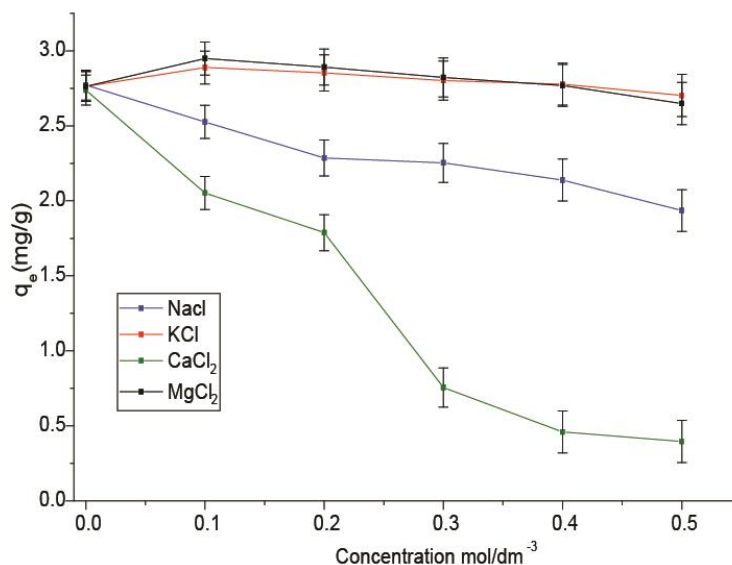
### Effect of pH

The pH of the dye solution plays a vital role in adsorption capacity (Hameed & Ahmad, 2009). The removal efficiency increased with increasing pH at lower adsorbent dosages (Figure 7). Lower adsorption at acid pH can be explained by the fact that the surface of the adsorbent was protonated. This would attract anions, and the excess of  $H^+$  ions would compete with the dye cations for adsorption sites (Shooto *et al.*, 2020). At higher pH values (6–12) the dye adsorption was almost constant when the adsorbent dosage was high. The presence of excess adsorption sites can explain this. In the range of pH 3–12, the effect of pH on the removal efficiency of a dosage of 1.0 g adsorbent in 100 mL MB dye solution was almost constant. Consequently, the effect of pH on this MB adsorption is evident.

As the  $pH_{ZPC}$  of laterite soil is approximately 6.6, when the pH of the solution is higher than 6.70, the surface of laterite would be negatively charged. As a result, cationic MB dye ions are attracted to laterite in aqueous solution by electrostatic forces of attraction (Hameed & Ahmad, 2009; Mouni *et al.*, 2018). Similar results have been obtained in previous studies of MB adsorption onto garlic peel (Hameed & Ahmad, 2009), kaolin (Mouni *et al.*, 2018), Agar/ $\kappa$ -carrageenan composite hydrogel (Duman *et al.*, 2018), and mucuna beans (Shooto *et al.*, 2020).

### Effect of ionic strength

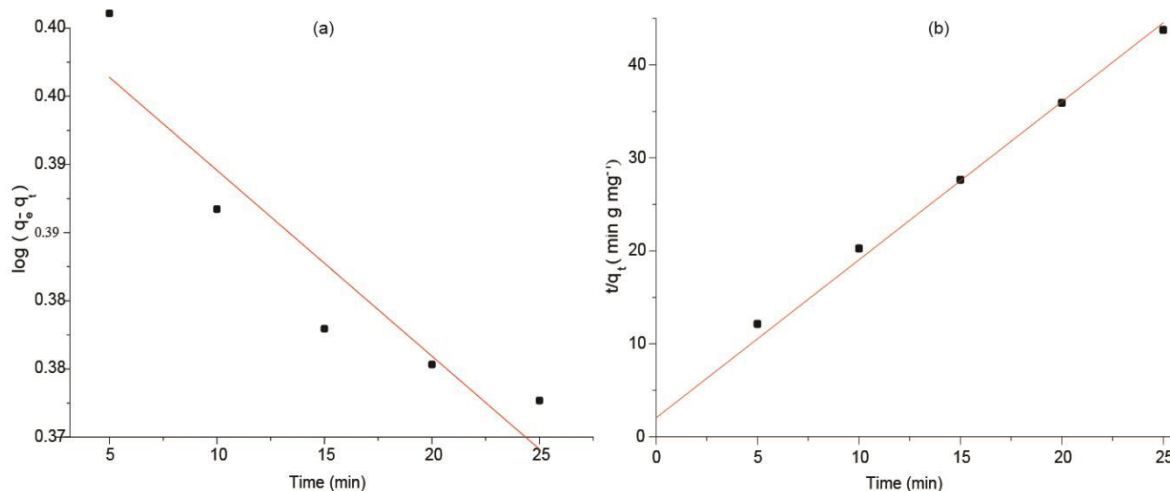
The effect of ionic strength on the dye uptake was studied by measuring  $q_e$  in the presence of the different salts NaCl, KCl,  $MgCl_2$ , and  $CaCl_2$ . Results indicated that an increase in the salt concentration decreased the dye's absorption into the laterite soil. KCl and  $MgCl_2$  showed similar effects on MB adsorption (Figure 8). Previous studies show that the presence of salt in the aqueous medium of the MB dye shields the electrostatic forces of opposite charges between the dye molecule and the adsorbent material, like laterite soil (Mouni *et al.*, 2018).



**Figure 8:** The effect of ionic strength on the MB removal efficiency,  $C_0 = 30$  mg/L,  $m = 1.0$  g,  $t = 60$  min. Volume of MB solution = 100 mL

### Adsorption kinetic studies

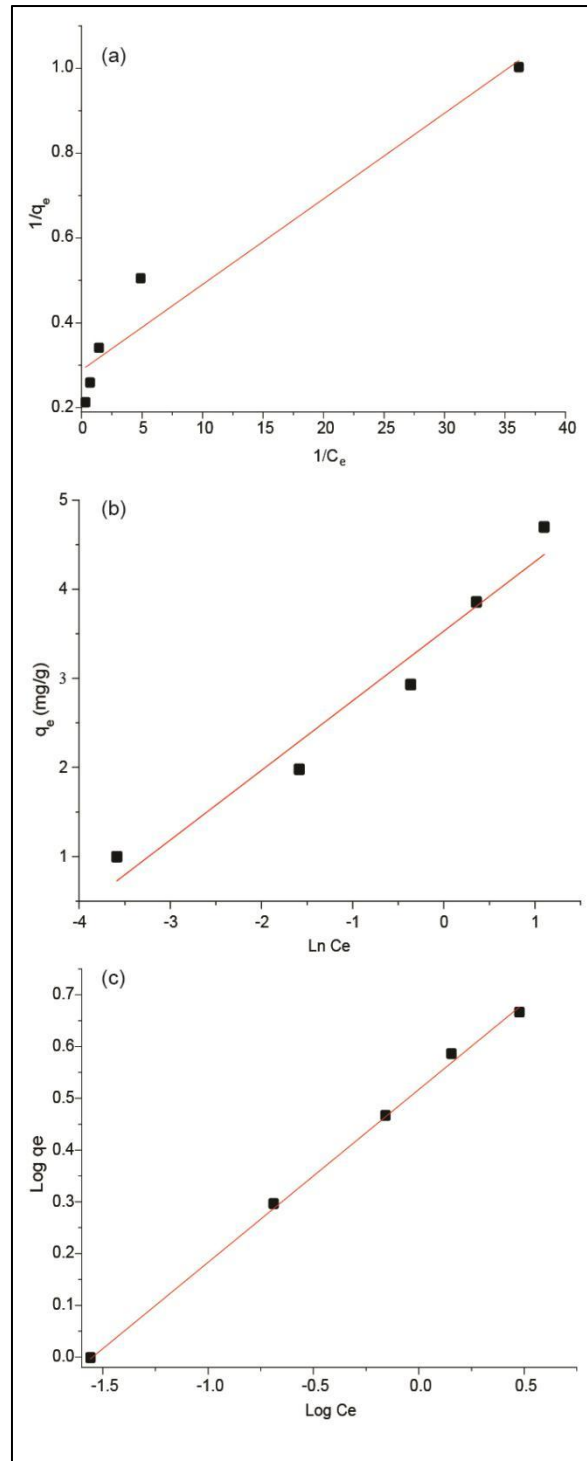
Kinetic models for the adsorption of MB on laterite clay provide useful pieces of evidence for efficiency and feasibility (Limousin *et al.*, 2007; Mouni *et al.*, 2018). In this study, the pseudo-first-order and pseudo-second-order rate equations were used. The pseudo-second-order equation provided an excellent fit, with a regression coefficient  $R^2 = 0.99$  (Figure 9). Moreover, the experimental  $q_e$  value (2.930 mg/g) was comparatively close to the calculated  $q_e$  value (2.974 mg/g) in the pseudo-second-order model, which further suggests the superiority of the said model over the pseudo-first-order kinetic models (Table 2). The kinetics of MB sorption on the raw laterite sorbent thus follows the pseudo-second-order rate expression. A good fit of experimental data with the pseudo-second-order model would indicate that chemical adsorption is the rate-controlling mechanism. This suggests that the rate-limiting step may involve valency forces through the sharing or exchange of electrons between sorbent and sorbate (Ho & McKay, 1999). Similar results have also been reported by other researchers where the pseudo-second-order kinetic model has shown good agreement with the experimental data for adsorption of MB dye (Franca *et al.*, 2009; Mouni *et al.*, 2018; Shooto *et al.*, 2020).



**Figure 9:** (a). Pseudo first order and (b). pseudo second-order kinetics of MB adsorption onto raw laterite

**Table 2:** Kinetic parameters for the removal of MB by raw laterite

$C_0$	Pseudo first order kinetics				Pseudo second order kinetics			
	$k_1$ ( $\text{min}^{-1}$ )	$q_{\text{exp}}$ (mg/g)	$q_{\text{cal}}$ (mg/g)	$R^2$	$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$q_{\text{exp}}$ (mg/g)	$q_{\text{cal}}$ (mg/g)	$R^2$
30 (mg/L)	$-5.44 \times 10^{-5}$	2.930	1.497	0.87	0.0558	2.930	2.974	0.99

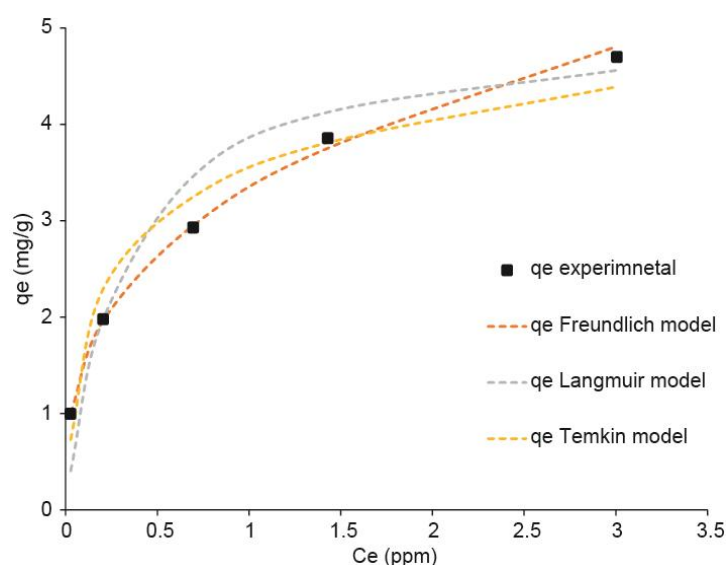
**Figure 10:** (a) Langmuir, (b) Temkin and (c) Freundlich isotherm for the sorption of MB dye on to raw laterite

## Adsorption isotherms

The adsorption characteristic equilibrium studies of laterite for MB removal from aqueous solutions were investigated. The experimental data fitted the Freundlich adsorption isotherm (Figure 10) with an  $R^2$  of 0.99, which means multilayer adsorption played a dominant role. The  $K_f$  value of the Freundlich isotherm model is  $3.33 \text{ L g}^{-1}$ . In addition, the experimental adsorption capacity ( $q_e$ ) is  $2.930 \text{ mg/g}$ , which is similar to the calculated adsorption capacity ( $2.949 \text{ mg/g}$ ) using the Freundlich isotherm model. The  $n$  value in the Freundlich model is 2.994 (between 1 and 10), indicating favourable MB adsorption by the laterite (Divband *et al.*, 2016). Similar results have been seen in studies carried out to remove MB (Shooto *et al.*, 2020). When the Langmuir isotherm model was considered, the data fitted with an  $R^2$  of 0.94. According to this model, the maximum monolayer adsorption capacity was calculated as  $3.46 \text{ mg/g}$ . The Temkin isotherm fitted with an  $R^2 = 0.96$  with a  $K_t$  value of  $91.73 \text{ (mg/g)}$  (Table 3). Furthermore, the experimental adsorption capacity data curve ( $C_e$  versus  $q_e$ ) was compared to the estimated adsorption capacities of the Langmuir, Freundlich, and Temkin isotherm models (Figure 11). These results indicate that the Freundlich isotherm model best fits the experimental adsorption capacity data, when compared with the Langmuir and Temkin isotherm models.

**Table 3:** Isotherm parameters for MB adsorption on to raw laterite

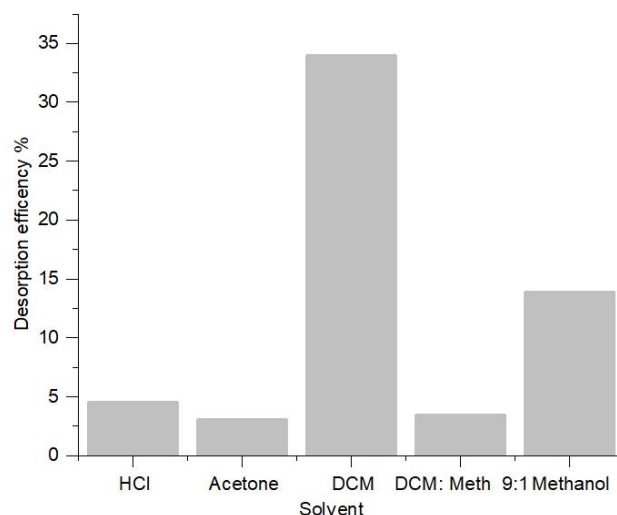
Model	Parameters	Value
Langmuir	$b \text{ (L mg}^{-1}\text{)}$	14.31
	$q_{\max} \text{ (mg/g)}$	3.46
	$R^2$	0.94
Freundlich	$K_f \text{ (L g}^{-1}\text{)}$	3.33
	$N$	2.99
	$R^2$	0.99
Temkin	$K_t \text{ (L mg}^{-1}\text{)}$	91.73
	$B \text{ (J mol}^{-1}\text{)}$	0.78
	$R^2$	0.96



**Figure 11:** Variation of experimental adsorption capacity curve and isotherm model adsorption capacity curves

## Desorption study

When considering the results of the desorption study, all solvents showed low desorption efficiencies (Figure 12). DCM resulted in the highest desorption efficiency of 33.89 %, whereas the lowest, 2.98%, was reported when acetone was used. Therefore, it can be said that laterite retains MB successfully after its adsorption from aqueous solutions. Regeneration is only efficient if the cost of regeneration is lower than the cost of production of the adsorbent (Ahmed *et al.*, 2016). In this case, as very small amounts of MB desorb from laterite in the case of all solvents, regeneration would not be efficient.



**Figure 12:** Effect of different solvents on the desorption of dye from MB loaded laterite soil

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## CONCLUSION

This study suggests that the laterite is an effective adsorbent for MB adsorption from an aqueous solution. The effect of pH for the removal efficiency of adsorbent dosage of 1.0 g was almost constant in the range of pH 3–12. As a result, the effect of pH on this MB adsorption can be justifiable. The removal of MB was initially rapid, and after 20 min, the rate of adsorption decreased. The optimum contact time and optimum dosage for removing MB from 100 mL of 30 mg/L dye solutions were obtained as 60 minutes and 1.0 g, respectively. The experimental data fitted well with the pseudo-second-order kinetic model, which suggests that chemical adsorption is the rate-controlling mechanism. The data also fitted the Freundlich isotherm model, which indicates that multilayer adsorption played a dominant role. Finally, our studies revealed that raw laterite is a cost-effective alternative for commercially available, expensive adsorbent material to remove methylene blue from aqueous solutions with an adsorption capacity of 2.930 mg/g.

When the adsorption capacities of the adsorbents used for MB removal are considered, raw laterite has a adsorption capacity of 2.930 mg/g, whereas bone charcoal has an adsorption capacity of 5 mg/g and fly ash has adsorption capacity of 5.718 mg/g (Kumar *et al.*, 2005). However, in the study, raw laterite was used to remove MB without any processing, demonstrating that this commonly available environmentally friendly material has the potential to remove MB from aqueous solutions.

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### Availability of data and material

The authors declare that all necessary data supporting the findings of this study are available within the article. If additional data supporting this study's findings are required, they can be made available from the corresponding author upon reasonable request.

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