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Insight into adsorption equilibrium, kinetics and thermodynamics of Malachite Green onto clayey soil of Indian origin

Papita Saha*, Shamik Chowdhury, Suyash Gupta, Indresh Kumar

Biotechnology Department, National Institute of Technology-Durgapur, Mahatma Gandhi Avenue, Durgapur, WB 713209, India

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ABSTRACT

This study investigates the adsorption potential of clayey soil of Indian origin to remove Malachite Green, a cationic dye from its aqueous solution. To this end, the effect of operational parameters including initial pH, adsorbent dose, contact time, initial dye concentration and temperature were studied in batch adsorption experiments. scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis were used to characterize the adsorbent material. The experimental equilibrium data were tested by three widely used isotherm models namely, Langmuir, Freundlich and Dubinin–Radushkevich (D–R). It was found that adsorption of Malachite Green on clayey soil correlated well with the Langmuir isotherm model, implying monolayer coverage of dye molecules onto the surface of the adsorbent. The maximum adsorption capacity was found to be 78.57 mg g^{-1} at 303 K. Kinetics of the adsorption process was tested by pseudo-first-order and pseudo-second-order kinetics, and intraparticle diffusion mechanism. Pseudo-second-order kinetic model provided a better correlation for the experimental data studied in comparison to the pseudo-first-order model. Intraparticle diffusion was not the sole rate-controlling factor. The activation energy of the adsorption process (E_a) was found to be 45.82 kJ mol^{-1} by using the Arrhenius equation, indicating chemisorption nature of Malachite Green adsorption onto clayey soil. A thermodynamic study showed spontaneous nature and feasibility of the adsorption process. A negative enthalpy (ΔH°) value indicated that the adsorption process was exothermic. The results indicate that clayey soil can be used as an effective and low-cost adsorbent to remove Malachite Green from aqueous solution.

1. Introduction

Colour is a visible pollutant and one of the most important hazardous species found in industrial effluents. The presence of dyes and pigments in water, even at very low concentrations, is highly undesirable [1]. More than 10,000 dyes are extensively used in many industrial processes such as textile, paper and plastics, leather, pharmaceutical, food, cosmetics, solvent, etc. [2–4]. As a result, considerable amount of coloured wastewater is generated. The discharge of dye-coloured wastewaters into the aquatic ecosystem represents both environmental and public health risks because of the negative ecotoxicological effects and bioaccumulation in wildlife. Most importantly, many dyes contained in wastewaters can decompose into carcinogenic aromatic amines under aerobic conditions which can cause serious health problems to humans and animals [5,6]. Also, dyes can cause allergy, dermatitis, skin irritation and cancer in humans [7]. Additionally, colour in surface water may affect photosynthesis by preventing light penetration, thereby compromising aquatic life [8].

Malachite Green (MG), an N-methylated diaminotriphenylmethane dye, and also called Basic Green 4 is the most widely used dye for colouring purpose among all other dyes of its category [9]. It is extensively used as a biocide in the aquaculture industry world-wide due to its high effectiveness against parasitic treatment, and fungal and bacterial infections in fish and fish eggs [10]. It is also used as a food colouring agent, food additive, a medical disinfectant and anthelminthic as well as a dye in silk, wool, jute, leather, cotton, paper and acrylic industries [11,12]. However there are several reports describing its hazardous and carcinogenic effects [13]. It is highly cytotoxic and carcinogenic to mammalian cells and acts as a liver tumor promoter. It decreases food intake capacity, growth and fertility rates; causes damage to liver, spleen, kidney and heart; inflicts lesions on skin, eyes, lungs and bones [14]. MG is also environmentally persistent and acutely toxic to a wide range of aquatic and terrestrial animals [10]. Therefore, the treatment of effluents containing such dye is of prime importance due to its harmful impacts on receiving waters.

The disposal of dye wastewater with proper treatment is a big challenge. This is mainly because synthetic dyes used in industries

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* Corresponding author. Tel.: +91 9903739855; fax: +91 3432547375.
E-mail addresses: papitasaha@gmail.com, papitasaha@yahoo.co.in (P. Saha).

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Nomenclature

A	Arrhenius constant
C_a	equilibrium dye concentration on the adsorbent ($mg\,L^{-1}$)
C_e	equilibrium dye concentration in solution ($mg\,L^{-1}$)
C_i	initial dye concentration ($mg\,L^{-1}$)
E	mean free energy ($kJ\,mol^{-1}$)
E_a	activation energy ($kJ\,mol^{-1}$)
ΔG°	Gibbs free energy change ($kJ\,mol^{-1}$)
ΔH°	enthalpy of reaction ($kJ\,mol^{-1}$)
h	initial adsorption rate ($mg\,g^{-1}\,min^{-1}$)
I	intraparticle diffusion model constant
K_C	distribution coefficient for adsorption
K_F	Freundlich constant ($mg\,g^{-1}$) ($L\,g^{-1}$)$^{1/n}$
K_L	Langmuir constant ($L\,mg^{-1}$)
k	rate constant
k_i	intraparticle diffusion rate constant ($mg\,g^{-1}\,min^{-0.5}$)
k_1	pseudo-first-order rate constant (min^{-1})
k_2	pseudo-second-order rate constant ($g\,mg^{-1}\,min^{-1}$)
m	weight of adsorbent (g)
n	Freundlich adsorption isotherm constant
q_e	equilibrium dye concentration on adsorbent ($mg\,g^{-1}$)
q_m	maximum adsorption capacity ($mg\,g^{-1}$)
q_t	amount of dye adsorbed at time t ($mg\,g^{-1}$)
R	universal gas constant (8.314 $J\,mol^{-1}\,K^{-1}$)
R^2	correlation coefficient
ΔS°	entropy of reaction ($J\,mol^{-1}\,K^{-1}$)
T	temperature (K)
V	volume of the solution (L)
Greek alphabets	
β	D–R isotherm constant ($mmol^2\,J^{-2}$)
ε	polanyi potential ($J\,mmol^{-1}$) $= RT\ln(1+1/C_e)$

are designed to resist fading upon exposure to sweat, heat, light, water, many chemicals including oxidizing agents, and microbial attacks [11,14]. The traditional methods for colour removal include photocatalytic degradation, sonochemical degradation, micellar enhanced ultrafiltration, cation exchange membranes, electrochemical degradation, integrated chemical–biological degradation, integrated iron(III) photoassisted-biological treatment, solar photo-Fenton and biological processes, and Fenton-biological treatment scheme [14]. However, all these methods have disadvantages like 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. It is defined as a process wherein a material is concentrated at a solid surface from its liquid or gaseous surroundings [15]. Adsorption separation in the environmental engineering is now an aesthetic attention and consideration abroad the nations, owning to its low initial cost, simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions [11]. Adsorption also does not result in the formation of harmful substances. A number of natural materials or the wastes/by-products of industries or synthetically prepared materials, which cost less and can be used as such or after some minor treatment have been tested and used for removal of MG from aqueous solutions [12,16–26]. However, low adsorption capacities of these adsorbents towards MG limit their applications in practical field. Hence attempts are made in this study to develop an inexpensive adsorbent for removal of MG from aqueous solutions using clayey soil. To our best knowledge, there is still no report about the use of natural clayey soil as adsorbent for MG.

Clayey soil is defined as soil that is composed of clay particles. Clays are distinguished from other particles present in soil such as silt by differences in size and mineralogy. Clay particles are characterized by their small size (particle size less than 0.002×10^{-3} m), flake or layered shape, high affinity for water, low porosity and slow diffusive transport [27]. Clay exhibit plasticity when mixed with water in certain proportions, become hard and firm when dried and converted into permanent rock like mass on firing. Clay particles are negatively charged and hence they attract and pick up positively charged particles. In the present study we report the very high adsorption potential of natural clayey soil of Indian origin for MG. Our previous findings indicate that rice husk; a readily available natural waste material could be employed as a cost-effective adsorbent in chemically modified form for the removal of MG from aqueous solutions [11]. In order to keep the cost of dye treatment low, natural clayey soil employed as adsorbent in the present study, was used without any pretreatment or other modification. The influence of various operating parameters such as initial dye concentration, contact time, adsorbent dose, temperature and initial pH of solution on MG adsorption was investigated by batch adsorption technique. SEM and XRD studies were carried out for the adsorbent characterization. The kinetics of the adsorption process was examined by fitting the experimental data with three kinetic models, i.e. pseudo-first-order, pseudo-second-order and intraparticle diffusion. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models were used to describe the adsorption equilibrium data. The activation energy (E_a) of the adsorption process was determined using the Arrhenius equation. The thermodynamic parameters, such as ΔG°, ΔH° and ΔS° were also deduced from the adsorption measurements in the present study, which are very useful in elucidating the nature of adsorption.

2. Materials and methods

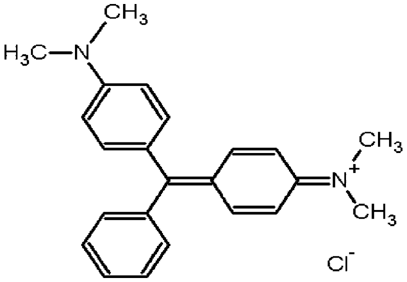
2.1. Adsorbent collection and preparation

Clayey soil used in this study was collected from the banks of river Matla owing to its high clay content and low permeability. The Matla river forms a wide estuary in and around the Sundarbans in South 24 Parganas district in the Indian state of West Bengal. The clayey soil sample was not purified prior to usage. It was initially sun-dried for 7 days followed by drying in hot air oven at 383 ± 1 K for 2 days. The dried soil was crushed and sieved to give a fraction of 100 mesh screen and then stored in sterile, closed glass bottles and used as an adsorbent.

2.2. Adsorbent characterization

The physico-chemical characteristics of the adsorbent were determined using standard procedures [27]. The % of clay, silt, and sand was analysed by hydrometric method [27].The cation exchange capacity (CEC) of the clayey soil sample was determined by the ammonium acetate method [28]. The BET surface area and pore size of the adsorbent were determined by Quantachrome NOVA 2200C USA, surface area and pore size analyzer. X-ray diffraction analysis of the adsorbent was carried out using Miniflex X-ray diffractometer equipment with a CuKα radiation source. In addition, scanning electron microscopy (SEM) analysis was carried out using a scanning electron microscope (Model Hitachi S-3000N) at 20 kV to study the surface morphology of the adsorbent. Prior to

Table 1
Details of the dye used.

Dyestuff	Basic Green 4 (BG 4)
IUPAC name	4-[(4-Dimethylaminophenyl)-phenyl-methyl]-N,N-dimethyl-aniline
Commercial name	Malachite Green (MG)
C.I. number	42,000
Appearance	Green crystalline powder
Empirical formula	$C_{23}H_{25}N_2Cl$
Molecular weight	365
Molecular structure	
λ_{max}	621 nm

scanning, the sample was coated with a thin layer of gold using a sputter coater to make it conductive

2.3. Preparation of adsorbate solutions

Malachite Green (MG) used in this study was of commercial quality and used without further purification. The detailed information of MG used in this study is given in Table 1. Dye stock solution (500 mg L^{-1}) was prepared by dissolving accurately weighed quantity of the dye in double distilled water. Experimental dye solution of different concentrations was prepared by diluting the stock solution with suitable volume of double distilled water.

2.4. Batch experiments

The batch tests were carried out in 250 mL glass-stoppered, Erlenmeyer flasks with 100 mL of working volume, with a concentration of 50 mg L^{-1}. A weighed amount (0.3 g) of adsorbent was added to the solution. The flasks were agitated at a constant speed of 150 rpm for 6 h in an incubator shaker (Model Innova 42, New Brunswick Scientific, Canada) at 303 ± 1 K. The influence of pH (2.0–10.0), initial dye concentration (10, 20, 40, 50, 60, 80, 100 mg L^{-1}), contact time (10, 20, 30, 40, 60, 90, 120, 180, 240 and 360 min), adsorbent dose (0.5, 1, 2, 3, 4, 5 g L^{-1}), and temperature (303, 313, 323, 333 K) were evaluated during the present study. Samples were collected from the flasks at predetermined time intervals for analyzing the residual dye concentration in the solution. The residual amount of dye in each flask was investigated using UV–vis spectrophotometer (Model Hitachi–2800). The amount of dye adsorbed per unit adsorbent (mg dye per g adsorbent) was calculated according to a mass balance on the dye concentration using Eq. (1):

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

The percent removal (%) of dyes was calculated using the following equation:

$$\text{Removal}\,(\%) = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

All adsorption experiments were performed in triplicate, and the mean values were used in data analysis. Control experiments, performed without the addition of adsorbent, confirmed that the sorption of dye on the walls of Erlenmeyer flasks was negligible.

3. Theory

3.1. Adsorption isotherms

An adsorption isotherm represents the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the adsorbent's surface at a given condition. A number of isotherms have been developed to describe equilibrium relationships. In the present study, the Langmuir [29,30], Freundlich [29,31] and Dubinin–Radushkevich (D–R) [29,32] models were used to describe the equilibrium data.

$$\text{Langmuir}: \frac{C_e}{q} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{3}$$

$$\text{Freundlich}: \log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \tag{4}$$

$$\text{Dubinin-Radushkevich (D-R)}: \ln q_e = \ln q_m - \beta\varepsilon^2 \tag{5}$$

3.2. Adsorption kinetics

In order to study the kinetics of the adsorption process, the pseudo-first-order [33,34], pseudo-second-order [33,35], and intraparticle diffusion kinetic model [33,14] were applied.

$$\text{Pseudo-first-order}: \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{6}$$

$$\text{Pseudo-second-order}: \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

$$\text{Intraparticle diffusion}: q_t = k_i t^{0.5} \tag{8}$$

3.3. Activation energy and thermodynamic parameters

The activation energy E_a for MG adsorption onto clayey soil was calculated by the Arrhenius equation [14,36]:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{9}$$

E_a can be determined from the slope of a plot of $\ln k$ versus $1/T$.

Thermodynamic behaviour of adsorption of MG on clayey soil was evaluated by the thermodynamic parameters – Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). These parameters were calculated using the following equations [11,14]:

$$\Delta G^\circ = -RT \ln K_C \tag{10}$$

$$K_C = \frac{C_a}{C_e} \tag{11}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{12}$$

A plot of ΔG° versus temperature, T will be linear with the slope and intercept giving the values of ΔH° and ΔS°

4. Results and discussion

4.1. Adsorbent characterization

The physical and chemical properties of clayey soil are presented in Table 2. The characteristics (Table 2) show that clayey soil has a high surface area, and most of the surface area (75%) is made up by pores smaller than 2 nm in pore width, the so-called micropores. The maximum of pores is found below 2 nm pore width. So, the particles are mostly microporous. X-ray diffraction spectrum of clayey soil sample is given in Fig. 1. Major components identified in clayey soil are quartz, illite, feldspar, kaolinite, montmorillonite, and calcite. The SEM micrograph of clayey soil is shown in Fig. 2. The surface structure of the adsorbent material is uneven, irregular

Table 2
Characteristics of the clayey soil used in this study.

Parameter	Value
pH	7.49
Moisture (%)	26.11
Liquid limit, w_L (%)	48
Plastic limit, w_P (%)	32
Plasticity index, I_p	24
Cation exchange capacity (mequiv./100 g dry soil)	31.82
Conductivity (μs/cm)	227
Permeability (m/s)	1.08×10^{-9}
BET surface area (m^2/g)	61
Average pore diameter (nm)	2.35
Micropore area (%)	75
Clay (%)	27
Silt (%)	68
Sand (%)	5

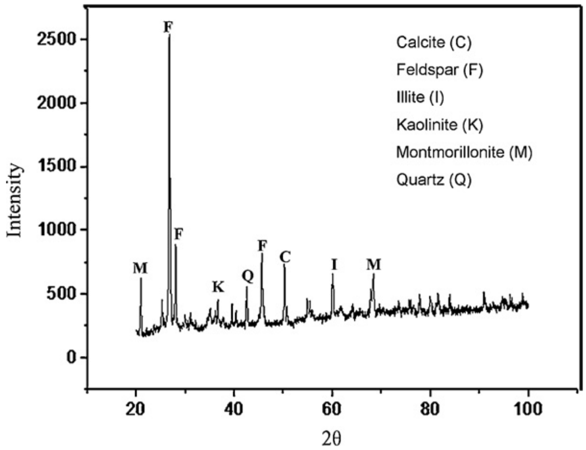


Fig. 1. XRD pattern of clayey soil.

and porous. The porous structure indicates that there was a good possibility for the dye molecules to be trapped and adsorbed onto the surface of the adsorbent.

4.2. *Effect of operating parameters*

4.2.1. *Effect of pH*

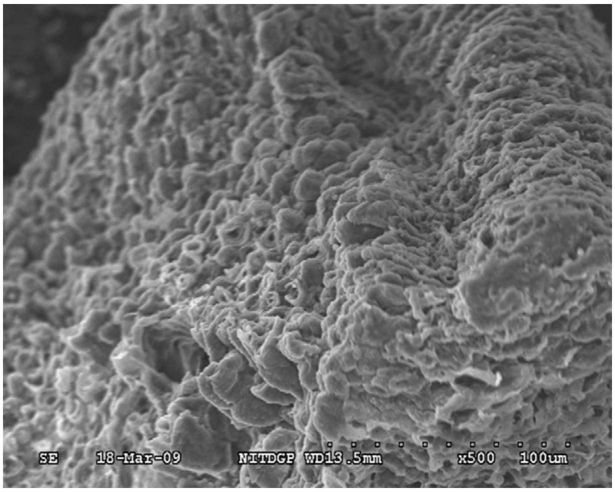


Fig. 2. SEM micrograph of clayey soil.

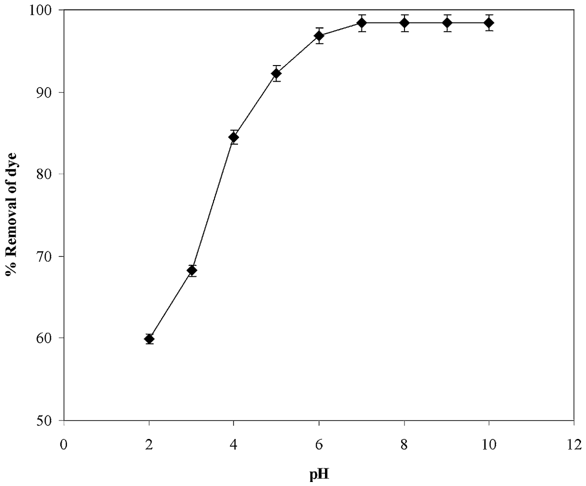


Fig. 3. Effect of pH on the adsorption of MG by clayey soil (experimental conditions: initial dye concentration: 50 mg L^{-1}, adsorbent dose: 0.2 g/0.1 L, agitation speed: 150 rpm, temperature: 303 K, contact time: 6 h).

The pH of an aqueous solution is an important monitoring parameter in dye adsorption, as it affects the surface charge of the adsorbent material and the degree of ionization of the dye molecule [37]. pH has also been associated with changes in the structural stability and colour intensity of the dye molecule. In addition, it is directly related with competition ability of hydrogen ions with adsorbate ions to active sites on the adsorbent surface [31]. The effect of pH on adsorption of MG onto clayey soil was evaluated in the pH range of 2.0–10.0. Percentage removal of the dye molecule as a function of pH is shown in Fig. 3. The removal of MG by clayey soil was noted to increase with the increase in pH of the dye solution, appreciably up to pH 6.0. A further increase in dye sorption between pH 6.0 and 10 was insignificant. Since the optimum pH for dye adsorption by clayey soil was found to be 6.0, this pH was used for further studies. MG is a cationic dye, which exists in aqueous solution in the form of positively charged ions. As a charged species, the degree of its adsorption onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which in turn is influenced by the solution pH. At low pH values, the protonation of the functional groups present on the adsorbent surface easily takes place, and thereby restrict the approach of positively charged dye cations to the surface of the adsorbent resulting in low adsorption of dye in acidic solution. With decrease in acidity of the solution, the functional groups on the adsorbent surface become de-protonated resulting in an increase in the negative charge density on the adsorbent surface and facilitate the binding of dye cations. The increase in dye removal capacity at higher pH may also be attributed to the reduction of H^+ ions which compete with dye cations at lower pH for appropriate sites on the adsorbent surface. However with increasing pH, this competition weakens and dye cations replace H^+ ions bound to the adsorbent surface resulting in increased dye uptake. Similar observation has been reported for sorption of MG onto degreased coffee bean [16].

4.2.2. *Effect of adsorbent dose*

Adsorbent dose is an important parameter influencing sorption processes since it determines the sorption capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. Fig. 4 shows the adsorption profile of MG versus different adsorbent concentration in the range of 0.5–5.0 g L^{-1}. It is observed that the percentage of dye removal increased with increase of adsorbent dose. Such a trend is mostly attributed to an increase in the sorptive surface area and the availability of more active adsorption sites [38]. Although the percentage removal of dye increased with increase of adsorbent dose, the equilibrium adsorption capacity for MG decreased with the increasing amount

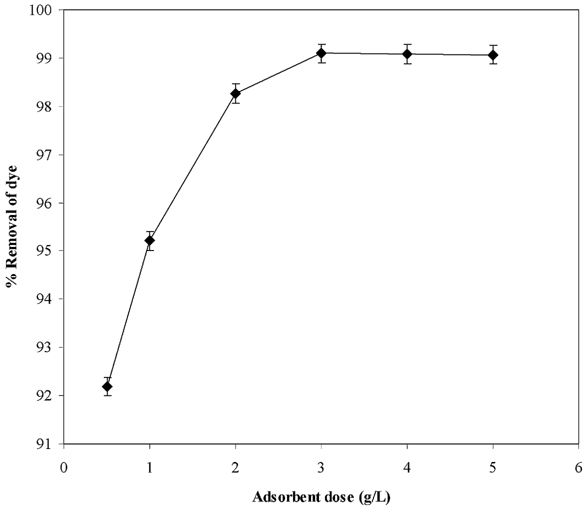


Fig. 4. Effect of adsorbent dose on adsorption of MG by clayey soil (experimental conditions: initial dye concentration: 50 mg L^{-1}, agitation speed: 150 rpm, pH: 6.0, temperature: 303 K, contact time: 6 h).

of adsorbent. This may be due to the decrease in total adsorption surface area available to dye molecules resulting from overlapping or aggregation of adsorption sites [9,5]. Thus with increasing adsorbent mass, the amount of dye adsorbed onto unit mass of adsorbent gets reduced, thus causing a decrease in q_e value with increasing adsorbent mass concentration. Further, maximum dye removal (99.09%) was observed at 3.0 g L^{-1} and further increase in adsorbent dose did not significantly change the adsorption yield. This is due to the binding of almost all dye molecules to adsorbent surface and the establishment of equilibrium between the dye molecules on the adsorbent and in the solution [5]. A similar trend has been reported for adsorption of MG by sawdust [39], and cyclodextrin-based adsorbent [9]. The optimum adsorbent dose was found to be 3.0 g L^{-1} and was used for the successive experiments.

4.2.3. *Effect of initial dye concentration*

The rate of adsorption is a function of the initial concentration of the adsorbate, which makes it an important factor to be considered for effective adsorption. The effect of different initial dye concentration on the adsorption of MG onto clayey soil is presented in Fig. 5. The percentage removal of dye decreased with increase in initial dye concentration and showed little decrease at higher concentrations. This can be explained that all adsorbents have a limited number of active sites, which become saturated at a certain concentration [10]. However, the adsorption capacity at equilibrium increased with increase in initial dye concentration. This is due to increasing concentration gradient, acts as increasing driving force to overcome all mass transfer resistances of the MG between the aqueous and solid phase, leading to an increasing equilibrium sorption until sorbent saturation is achieved [16]. Similar results were reported for adsorption of MG from aqueous solution onto chemically modified rice husk [11].

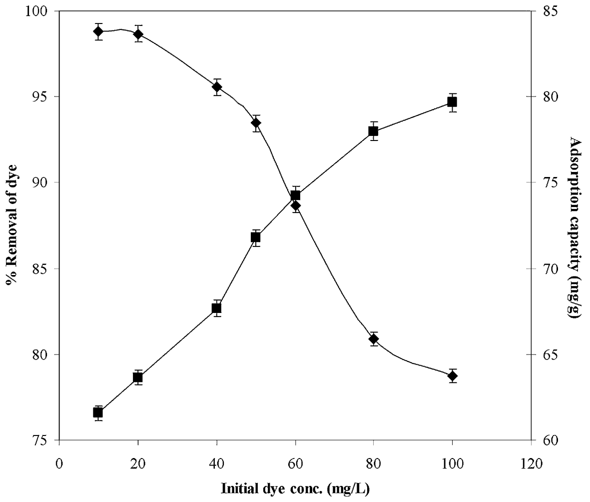


Fig. 5. Effect of initial dye concentration on adsorption of MG by clayey soil (experimental conditions: adsorbent dose: 0.3 g/0.1 L, agitation speed: 150 rpm, pH: 6.0, temperature: 303 K, contact time: 6 h).

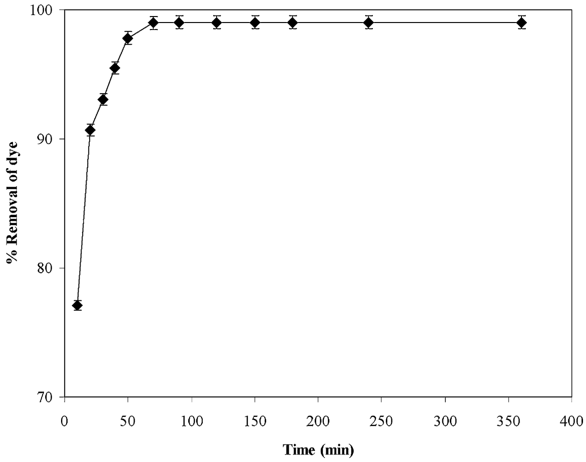


Fig. 6. Effect of contact time on adsorption of MG by clayey soil (experimental conditions: initial dye concentration: 50 mg L^{-1}, adsorbent dose: 0.3 g/0.1 L, agitation speed: 150 rpm, pH: 6.0, temperature: 303 K).

4.2.4. *Effect of contact time*

It is essential to evaluate the effect of contact time required to reach equilibrium for designing batch adsorption experiments. Therefore the effect of contact time on adsorption of MG was also investigated. The uptake of MG as a function of contact time is shown in Fig. 6. As illustrated in Fig. 6, adsorption of MG increased with rise in contact time up to 60 min. Further increase in contact time did not enhance the dye adsorption process. The adsorption process attained equilibrium after 90 min. The fast adsorption rate at the initial stage may be explained by an increased availability in the number of active binding sites on the adsorbent surface. The sorption rapidly occurs and normally controlled by the diffusion process from the bulk to the surface. In the later stage, the sorption is likely an attachment-controlled process due to less available sorption sites. Similar findings for MG adsorption onto other natural adsorbents have been reported by other investigators [40–42].

4.2.5. *Effect of temperature*

It is well established that temperature is an additional factor greatly influencing any adsorption process. Therefore, batch adsorption experiments were carried out at different temperatures ranging from 303 to 333 K. Data obtained from the experiments are presented in Fig. 7. The results clearly indicate that MG uptake decreased with increase in temperature. The observed decrease in the adsorption capacity with increase of temperature from 303 to 333 K indicates that low temperature favours the removal of MG molecules by adsorption onto clayey soil. These results indicate that the adsorption process is exothermic in nature. At high temperature the thickness of the boundary layer decreases due to increased tendency of the dye molecules to escape from the adsorbent surface to the solution phase, which results in a decrease in the adsorption capacity as temperature is increased [43]. Similar results were pre-

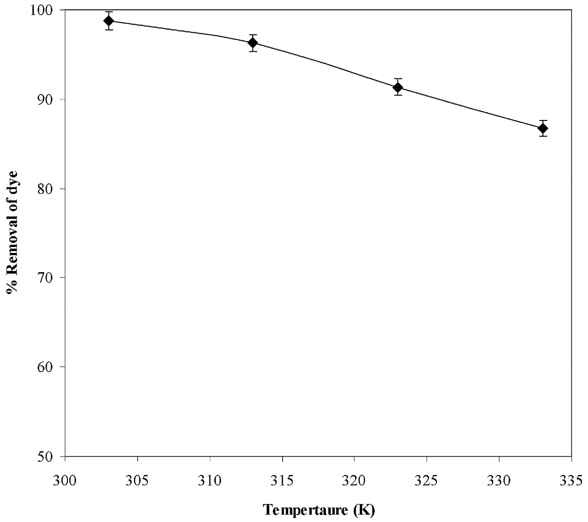


Fig. 7. Effect of temperature on adsorption of MG by clayey soil (experimental conditions: initial dye concentration: 50 mg L^{-1}, adsorbent dose: 0.3 g/0.1 L, agitation speed: 150 rpm, pH: 6.0, contact time: 6 h).

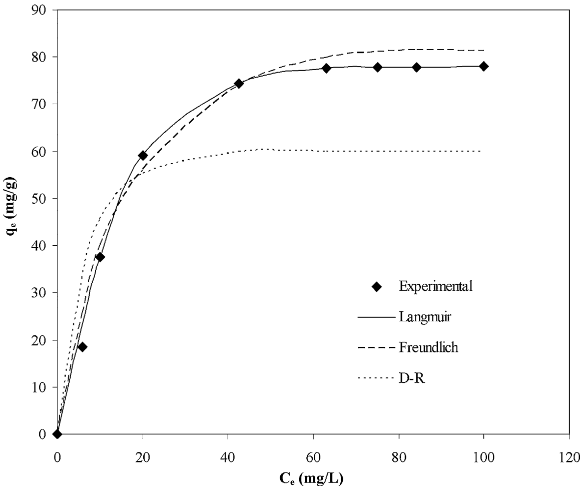


Fig. 8. Comparison between the measured and modeled isotherm profiles for the adsorption of MG by clayey soil (experimental conditions: initial dye concentration: 50 mg L^{-1}, adsorbent dose: 0.3 g/0.1 L, agitation speed: 150 rpm, pH: 6.0, temperature: 303 K).

viously reported by Chowdhury and Saha [14] on adsorption of MG on sea shell powder.

4.3. Adsorption isotherms

As already mentioned, the Freundlich, the Langmuir, and the Dubinin–Radushkevich (D–R) isotherm models were used to describe the equilibrium adsorption data of MG onto clayey soil; and the modelled adsorption isotherms are plotted in Fig. 8. The parameters and correlation coefficients obtained from the plots of Langmuir (C_e/q_e versus C_e), Freundlich ($\log q_e$ versus $\log C_e$) and D–R ($\ln q_e$ versus ε^2) (figures not shown) are listed in Table 3.

As can be seen from Table 3, the Langmuir isotherm model showed excellent fit to the experimental data with high correlation coefficients at all temperatures. The maximum dye sorption capacity of clayey soil was found to be 78.57 mg g^{-1} at 303 K. The values of K_L and q_m decreased with increase in temperature, indicating that increasing temperature induced a lower maximum adsorption capacity.

The empirical Freundlich model also showed a fairly good fit to the experimental equilibrium data at all temperatures studied ($R^2 > 0.97$). The sorption capacity, K_F decreased with increase in temperature (Table 3) which implies that the sorption process was exothermic in nature. The magnitude of n gives a measure of favourability of adsorption. The values of n between 1 and 10 (i.e., $1/n$ less than 1) represents a favourable sorption. For the present study the value of n also presented the same trend representing a beneficial sorption.

In order to distinguish between physical and chemical biosorption on the heterogeneous surfaces the equilibrium data were tested with the D–R isotherm model. The correlation coefficients were found to be lower than the Freundlich and Langmuir isotherm models (Table 3). The constant β gives an idea about the mean free energy E (kJ mol^{-1}) of adsorption per mole of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship [44]:

$$E = \frac{1}{\sqrt{2\beta}} \tag{13}$$

The value of this parameter can give information about the type of adsorption mechanism. If the magnitude of E is between 8 and 16 kJ mol^{-1}, the sorption process is supposed to proceed via chemisorption, while for values of $E < 8$ kJ mol^{-1}, the sorption process is of physical nature [44]. The magnitude of E were higher than 8 kJ mol^{-1} for all studied temperatures, indicating that adsorption mechanism of MG onto clayey soil was chemisorption.

In comparing the linear correlation coefficients of the three isotherms listed in Table 3, it can be concluded that adsorption of MG onto clayey soil best fitted to the Langmuir isotherm equation under the temperature range studied. The fitness of the adsorption data to the Langmuir isotherm implies that the binding energy on the whole surface of the adsorbent was uniform and that sorbate–sorbate interaction was negligible. It also indicates that the adsorbed dye molecules did not interact or compete with each other and that they were adsorbed by forming a monolayer. Table 4 summarizes the comparison of the maximum MG adsorption capacities of various sorbents including clayey soil. The comparison shows that clayey soil has higher adsorption capacity of MG than many of the other reported adsorbents, reflecting a promising future for clayey soil utilization in MG removal from aqueous solutions.

4.4. Adsorption kinetics

In the present investigation, three kinetic models namely, pseudo-first-order, pseudo-second-order and intraparticle diffu-

Table 3
Adsorption isotherm constants for adsorption of MG onto clayey soil at different temperatures.

T (K)	Langmuir isotherm parameters			Freundlich isotherm parameters			D–R isotherm parameters			
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F (mg g^{-1}) (L mg^{-1})$^{1/n}$	$1/n$	R^2	q_m (mg g^{-1})	β (mmol^2 J^{-2})	E (kJ mol^{-1})	R^2
303	78.574	0.845	1.0000	11.263	3.878	0.9834	71.487	2.45×10^{-9}	14.276	0.9176
313	75.798	0.712	1.0000	10.339	3.614	0.9782	67.912	2.57×10^{-9}	13.926	0.9187
323	72.261	0.624	0.9999	8.401	3.495	0.9769	65.238	2.64×10^{-9}	13.751	0.9113
333	70.184	0.538	0.9999	7.874	3.147	0.9752	62.569	2.79×10^{-9}	13.366	0.9145

Table 4
Comparison of MG adsorption capacity of clayey soil with other reported low-cost adsorbents.

Sorbent	q_{max} (mg g^{-1})	Reference
Arundo donax root carbon	8.69	[45]
Waste apricot	116.27	[46]
Activated charcoal	0.179	[47]
Tamarind fruit shell	1.951	[12]
Activated carbons commercial grade	8.27	[18]
Laboratory grade activated carbons	42.18	[18]
Bentonite	7.72	[19]
Sugarcane dust	4.88	[20]
Degreased coffee bean	55.3	[16]
Hen feathers	26.1	[21]
Iron humate	19.2	[22]
Rubber wood sawdust	36.45	[23]
Cellulose	2.422	[24]
Maize cob powder	37.037	[48]
Rattan sawdust	62.7	[49]
Treated sawdust	65.8	[41]
Neem leaf powder	133.6	[25]
Ricinus communis	27.78	[26]
Lemon peel	51.73	[50]
Clayey soil	78.57	This study

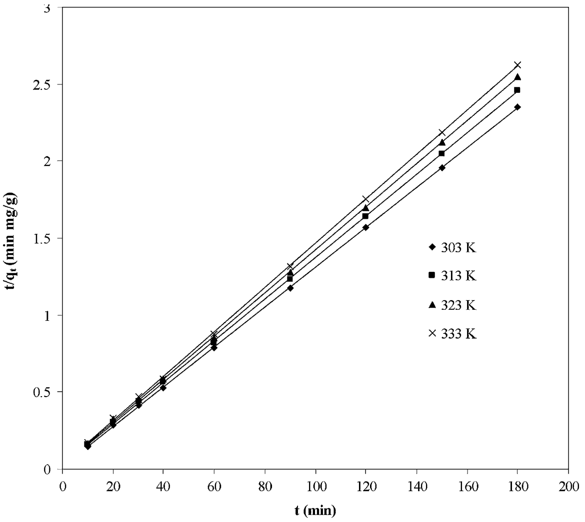


Fig. 9. Pseudo-second-order kinetic plots for adsorption of MG onto clayey soil at different temperatures (experimental conditions: initial dye concentration: 50 mg L^{-1}, adsorbent dose: 0.3 g/0.1 L, agitation speed: 150 rpm, pH: 6.0).

sion model were tested to obtain rate constants, equilibrium adsorption capacity and adsorption mechanism at different temperatures.

The pseudo-first-order rate constant, k_1, and the equilibrium adsorption capacity, q_e at different temperatures were determined from the slope and intercept of the plots of log ($q_e - q_t$) versus t (figure not shown) and are listed in Table 5 along with the correlation coefficient, R^2. From the kinetic data in Table 5, it can be seen that at all studied temperatures, the correlation coefficients for the pseudo-first-order kinetic model are very low. Moreover, a large difference between theoretical and experimental equilibrium adsorption capacity, q_e is observed at all temperatures, indicating a poor fit of the pseudo-first-order equation to the experimental data.

The kinetic data of MG adsorption onto clayey soil was further analyzed using the pseudo-second-order equation (Eq. (8)). The pseudo-second-order model constants were determined from the slope and intercept of the plot of t/q_t versus t. The plot of t/q_t against t at different temperatures is shown in Fig. 9. Contrary to the pseudo-first-order equation, the fitting of the kinetic data in the pseudo-second-order equation showed excellent linearity with high correlation coefficient ($R^2 > 0.999$) over the temperature range of 303–333 K. The data obtained for the pseudo-second-order kinetic model at the four different temperatures is tabulated in Table 5. An analysis of the data in Table 5 suggests that the kinetics of adsorption of MG on clayey soil can be explained more accurately by the pseudo-second-order kinetic model. It is also observed from Table 5 that rate constant, k_2 decreased as the temperature increased indicating exothermic nature of adsorption of MG onto clayey soil. Furthermore, the calculated q_e values were found to be quite close to the experimental q_e values at all the temperatures studied (303–333 K). So, it was inferred that the adsorption of MG on clayey soil followed pseudo-second-order kinetics. This finding suggests that the rate-limiting step of the adsorption system may be chemisorption. A similar phenomenon was also observed in adsorption of MG onto degreased coffee bean [16], bentonite [19] and Arundo donax root [45]. From, the pseudo-second-order kinetic parameters, the initial adsorption rate, h (mg g^{-1} min^{-1}) at different temperatures was calculated using Eq. (14) [35] and are presented in Table 5.

$$h = k_2 q_e^2 \tag{14}$$

As evident from Table 5, the initial adsorption rate, h, decreased with increase in temperature suggesting that adsorption of MG onto clayey soil was not favourable at higher temperatures.

The intraparticle diffusion was investigated using the empirical relationship based on the model of Weber–Morris (Eq. (8)). The Weber–Morris plots (q_e versus $t^{0.5}$) for adsorption of MG on clayey soil at different temperatures were multimodal with three distinct regions (figure not shown). The initial curved region corresponds to the external surface uptake, the second stage relates the gradual uptake reflecting intraparticle diffusion as the rate limiting step and final plateau region indicates equilibrium uptake. Based on these results it might be concluded that intraparticle diffusion was involved in MG adsorption onto clayey soil, but it was not the sole rate determining step and that some other mechanisms also play an important role. Similar trend has already been reported for MG adsorption onto different low cost adsorbents [14,45,51].

4.5. Activation energy and thermodynamic parameters

From the pseudo-second-order rate constant k_2 (Table 5), the activation energy E_a for adsorption of MG onto clayey soil was determined using the Arrhenius equation (Eq. (9)). By plotting ln k_2 versus $1/T$ (Fig. 10), E_a was obtained from the slope of the linear plot. The value of E_a for MG adsorption on clayey soil was 45.82 kJ mol^{-1}. The magnitude of activation energy may give an idea about the type

Table 5
Kinetic parameters for adsorption of MG onto clayey soil.

T (K)	$q_{e,exp}$ (mg g^{-1})	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			
		$q_{e,cal}$ (mg g^{-1})	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	R^2
303	76.295	58.964	0.0745	0.9625	76.486	0.01268	74.179	1.0000
313	73.511	54.245	0.0597	0.9638	74.197	0.00782	43.050	0.9999
323	70.269	51.577	0.0343	0.9611	70.856	0.00451	22.642	0.9999
333	68.834	48.754	0.0196	0.9576	69.293	0.00245	11.763	0.9999

Table 6
Activation energy and thermodynamic parameters for adsorption of MG onto clayey soil.

E_a (kJ mol^{-1})	ΔG° (kJ mol^{-1})				ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
	303 K	313 K	323 K	333 K		
45.82	−14.72	−12.35	−9.39	−7.34	−90.76	−251.00

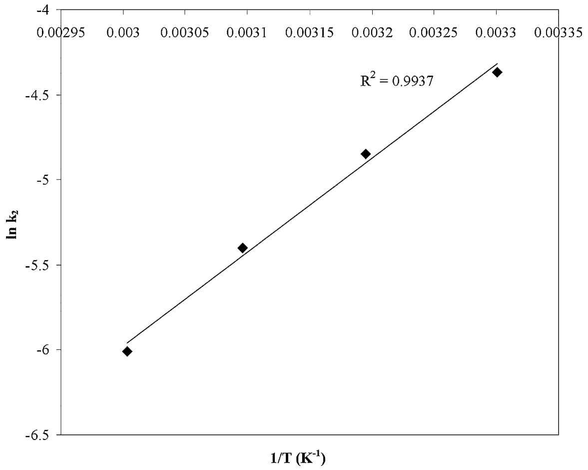


Fig. 10. Arrhenius equation plot for adsorption of MG onto clayey soil.

of sorption. There are two main types of adsorption: physical and chemical. The activation energy for physical adsorption is usually less than 40 kJ mol^{-1}, since the forces involved in physical adsorption are weak. Higher values represent chemical reaction process as chemical adsorption is specific and involves forces much stronger than in physical adsorption [52]. In the present study, the value of the activation energy confirms that the nature of MG adsorption onto clayey soil is chemisorption. The finding is in accordance with the observations of Chowdhury et al. [11] on adsorption of MG onto chemically modified rice husk.

The Gibb's free energy (ΔG°) for adsorption of MG onto clayey soil at all temperatures was obtained from Eq. (10) and are presented in Table 6. The values of ΔH° and ΔS° were determined from the slope and intercept of the plot of ΔG° versus T (Fig. 11) and are also listed in Table 6. The negative value of ΔG° at all temperatures indicates the feasibility of the process and the spontaneous nature of the dye adsorption onto clayey soil. Increase in value of ΔG° with increase in temperature suggests that lower temperature makes the adsorption easier. The negative value of ΔH° implies that the adsorption phenomenon is exothermic. The magnitude of ΔH° may give an idea about the type of sorption. The heat evolved during physical adsorption is of the same order of magnitude as the heats of condensation, i.e., 2.1–20.9 kJ mol^{-1}, while the heats of chemisorption generally falls into a range of 80–200 kJ mol^{-1} [53]. Therefore, MG adsorption by clayey soil may be attributed to a chemical adsorption process. The negative value of ΔS° suggests that the process is enthalpy driven.

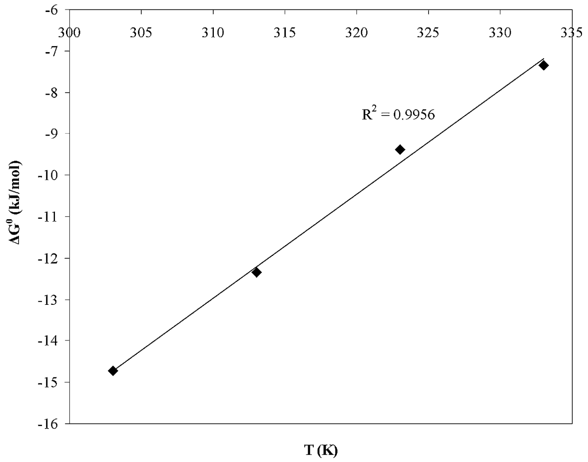


Fig. 11. Plot of Gibb's free energy change versus temperature for adsorption of MG onto clayey soil.

4.6. *Cost analysis*

Adsorbent cost is an important parameter for comparing the industrial application of adsorbent materials; however it is seldom reported in the literature [11]. The overall cost of the adsorbent material is governed by several factors which include its availability (whether it is natural, industrial/agricultural/domestic wastes or by-products or synthesized products), the processing required and reuse [11]. Clayey soil is available in abundance and collected at river beds at no cost; however the handling charges for the collection and transportation will be involved. The most popular commercial adsorbent of the present time for the removal of MG is activated charcoal. In India the cheapest variety of the commercial activated charcoal costs around 1000 INR per kg. Compared to activated charcoal, the total cost of natural clayey soil is extremely low. However, the fate of the adsorbent material after complete utilization is a relatively unanswered question. It is suggested that the final adsorbent may be disposed via land-fill or by incineration. Thus the use of clayey soil as an adsorbent is a thoughtful and economic attempt for its valuable, necessitous and needy utilization for wastewater treatment processes.

5. Conclusion

In this study, natural clayey soil of Indian origin was tested and evaluated as a possible adsorbent for removal of MG, a cationic dye from its aqueous solution using batch sorption technique. The adsorption studies were carried out as a function of solution pH, adsorbent dosage, contact time, initial dye concentration and temperature. Percentage removal of the dye molecule decreased with an increase in the initial dye concentration while it increased with increase in contact time and adsorbent dose up to a certain level. The maximum adsorption occurred at pH 6.0. Experimental equilibrium data provided best fit with the Langmuir isotherm model, indicating monolayer sorption on a homogenous surface. The monolayer sorption capacity decreased with increase in temperature in the range 303–333 K. The maximum monolayer sorption capacity at 303 K was estimated to be 78.57 mg.g^{-1}. Sorption of MG on clayey soil seems to be favourable process. According to Dubinin–Radushkevich (D–R) isotherm model, adsorption of MG onto clayey soil was chemisorption. The adsorption kinetics followed pseudo-second-order kinetic model indicating towards chemisorption. Intra-particle diffusion was not the sole rate-controlling factor. The activation energy of the adsorption process (E_a) was found to be 45.82 kJ mol$^{-\mathbf{1}}$ by using the Arrhenius equation, indicating chemisorption nature of MG adsorption onto clayey soil. Thermodynamic parameters such as change in Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were also estimated.

Thermodynamic analysis suggests that removal of MG from aqueous solution by clayey soil was a spontaneous and exothermic process. The present findings suggest that clayey soil may be used as an inexpensive and effective adsorbent without any treatment or any other modification for the removal of MG from aqueous solutions

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