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P. Monash[a]; G. Pugazhenthi[a]
[a] Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati, India

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Removal of Crystal Violet Dye from Aqueous Solution Using Calcined and Uncalcined Mixed Clay Adsorbents

P. Monash and G. Pugazhenthi
Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati, India

In this work, calcined and uncalcined mixed clays containing kaolin, ball clay, feldspar, pyrophyllite, and quartz are examined as a potential adsorbent for the removal of crystal violet dye from aqueous solution. These clays are characterized by nitrogen adsorption/desorption isotherms, X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, and thermo gravimetric analysis (TGA). The kinetics and thermodynamic parameters as well as the effects of the pH, the temperature, and the adsorbent dosage have also been investigated. The experimental results indicate that the Langmuir model expresses the adsorption isotherm better than the Freundlich model. The obtained result showed a tremendous increase in the crystal violet adsorption capacity ($1.9 \times 10^{-3}\,\mathrm{mol\,g^{-1}}$) after calcination, which is one order greater than that of the uncalcined mixed clay. The mechanism of the adsorption process is elucidated on the basis of experimental data. The percentage removal of crystal violet dye increases with increasing the pH, the temperature, and the adsorbent dosage. The investigation of kinetic studies indicates that the adsorption of crystal violet on calcined and uncalcined mixed clays could be described by the pseudo-second-order model. The negative ΔG^0 values obtained from the thermodynamic investigation confirm that the adsorption is spontaneous in nature. The adsorption results suggest that the calcined and uncalcined mixed clays can also be used as low cost alternatives to the expensive activated carbon for the removal of dyes from aqueous solution.

Keywords adsorption; calcined; clay; crystal violet; isotherm; thermodynamic

INTRODUCTION

The carcinogenic and the toxic nature of the dye stuff effluent discharged from industries such as textile, paper, carpet, printing, leather industries, etc., creates harmful effects on aquatic life and human beings (1). It also causes death to the soil microorganism that affects the agricultural productivity (2). Because of the aforesaid reasons, the treatment of the dye stuff effluents is an important concern which creates lots of environmental issues. The treatment of dyes is broadly classified into three categories, namely, biological, chemical, and physical treatment. Although all the treatment methods have their own merits and demerits, adsorption is most widely adopted for the treatment of dyes because of its effectiveness and versatility (3,4). Many adsorbents have been tested to reduce dye concentrations from aqueous solutions (4,5). Among the various adsorbents, activated carbon is the most widely used adsorbent for industrial applications because of its high adsorption capacity (6). Unfortunately, it is too expensive and difficult to regenerate. So the researchers are being focused to search for alternative low cost and abundantly available adsorbents having high adsorption capacity. Many low-cost adsorbents, including natural materials, clays, biosorbents, etc., were utilized for the removal of the dyes (4–12). Among these adsorbents, clays have found to be a more interesting adsorbent for adsorption studies due to its low cost, higher surface charges, and good lamellar structure, which makes it a potential adsorbent for the treatment of heavy metals, dyes, and organic compounds from water and wastewater. Generally, clays are aggregates of hydrous siliceous particles containing a variety of phyllosilicate minerals rich in silicon and aluminum in the form of oxides and hydroxides, which includes variable amounts of structural water. The interlayer pore opening of the clays depends on the nature, size, and shape of intercalated species. Depending on their origin and treatment methods, clays behave differently and follow different adsorption mechanism leads to different adsorption capacity of the dye molecules (11–13).

Smectite and kaolinite group of clays were most widely used for the adsorption of dyes and heavy metals. Smectite clay has a 2:1 expanding crystal lattice made up of two tetrahedral sheets with a central Al octahedral sheet. Montmorillonite, bentonite, beidellite, nontronite (dioctahedral) and hectorite, saponite, and sauconite (trioctahedral) belong to the smectite group. Kaolinite clay is also called as kaolin, which is a 1:1 aluminosilicate formed by a layer of silica ring joined to a layer of alumina octahedra through shared oxygen. Kaolinite, dickite, nacrite, halloysite (dioctahedral) and antigorite, chamosite, chrysotile, cronstedite (trioctahedral) are layers of the kaolinite group.

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Address correspondence to G. Pugazhenthi, Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati 781039, Assam, India; Fax: +91 361 2582291. E-mail: pugal@iitg.ac.in

The different minerals are polymorphs i.e., the minerals have the same chemistry but different structures play a vital role in adsorption. In general, most of the clays have permanent negative charges, which is due to the isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer (14). Clays are widely used for the adsorption of cationic dyes without any surface modification due to its permanent negative charges. However, for the adsorption of anionic dyes, surface modification is required to achieve a good adsorption capacity and the recent research works suggested that modified clay minerals are innovative and promising adsorbent material for anionic dye treatment (1,6,8,10,11,13,15–17). Akbal (18) has investigated the adsorption of methylene blue (MB) and crystal violet (CV) on pumice powder having two different compositions. The pumice-II powder containing SiO_2:Al_2O_3 ratio of 3.87 showed a higher adsorption capacity than pumice-I (SiO_2:Al_2O_3 ratio = 4.81). In addition, both the pumice powders have also shown the higher adsorption capacity for methylene blue than crystal violet. Eren and Afsin (19,20) have investigated CV adsorption on raw, base-activated, and Al-saturated sepiolite clay as well as on raw, Ni-saturated (Ni-), Co-saturated (Co-), and Zn-saturated (Zn-) bentonite surfaces. They concluded that an increase/decrease in the adsorption capacity of cation-saturated/base activated sepiolite or bentonite was attributed to an increase/decrease in the permanent charges at the basal surface. Rytwo et al. (21) studied the interactions between monavalent organic cationic dyes on montmorillinite and a model was simulated considering the electrostatic and specific binding concept.

Several authors have also reported the adsorption of dyes on different clays such as kaolin (8), palygorskite (9), attapulgite (10), hectorite(11), pyrophyllite (17), pumice (18), sepiolite (19), bentonite (20), montmorillonite (21) etc. Only few works has been reported for the removal of dyes on raw and calcined adsorbents (22–24). The reactions/phase transformations during calcination may change the surface charges and also creates different voids within the given plane that may enhance the adsorption capacity of dye on the clay surface. Only few explanations were available regarding the mechanisms for the adsorption of dyes on clay. It seems to be necessary to study the adsorption mechanism of dyes on the external and interlamellar surfaces of the clays for complete understanding. A critical review of the literatures conveys that the adsorption of dyes on mixed clay containing aluminosilicates has not yet been tried.

The purpose of the present study is to investigate the possibility of using mixed clay containing kaolin, ball clay, feldspar, pyrophyllite, and quartz for the removal of crystal violet dye by batch adsorption method. The fact of using the aforesaid clays is that, it is inexpensive and most widely used for pottery works (it may be used for this purpose after adsorption). The raw (uncalcined) clay is calcined at 900°C to study the effect of calcination on adsorption of crystal violet dye. The characteristics of both calcined and uncalcined mixed clays are analyzed. In addition to adsorption equilibrium studies, thermodynamic and kinetic investigations are also made for the adsorption of crystal violet dye on both the adsorbents. The effect of temperature, the pH, and the adsorbent dosage on adsorption capacity is also examined. Moreover, an attempt has been made to explain the adsorption mechanism of dye on clay in terms of interbasal spacing and its functional groups.

MATERIALS AND METHODS

Crystal violet dye (C.I. 42555, chemical formula = $C_{25}H_{30}N_3Cl$, Mol. wt. = 407.99) was purchased from Loba Chemie (Mumbai, India). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were procured from Merck (I) Ltd (Mumbai, India). All the chemicals were used as received. Water used in the preparation of dye solution was obtained from the Millipore System.

Preparation of Mixed Clay Adsorbent

The low cost clays used in the present work were collected locally. All the clays (kaolin, ball clay, feldspar, pyrophyllite, and quartz) were mixed in a ball mill for 40 min at 40 rpm and sieved through a 200-mesh standard sieve. The molar composition of the raw mixed clay was in the ratio of 19.70 Al_2O_3: 42.67 SiO_2: 0.027 Na_2O: 4.32 H_2O: 1.0 CaO (calculated using formula weights). The mixed clays of a given composition were stirred with Millipore water in a Borosil beaker for 3 hours and then the mixture was kept undisturbed for 30 to 60 min and the suspended impurities was removed. The above process was repeated several times by adding Millipore water to get rid off the impurities from the mixed clay. Finally, the mixed clay was dried in a hot air oven at 120°C to remove the moisture. The raw mixed clay was obtained by drying a part (half of the total amount) of the above mixed clay at 150°C and stored in an air tight bottle. The second half of the above mixed clay was calcined at 900°C for 6 h to get the calcined mixed clay. The heating and the cooling rate of the calcination process was controlled at 2°C min^{-1} using a programmable muffle furnace. Both the calcined and uncalcined mixed clay was tested for the adsorption of crystal violet dye.

Characterization of Adsorbent

Thermo gravimetric analysis (TGA) was performed on the Mettler Toledo thermo gravimetric analyzer (TGA/SDTA 851® model) under air atmosphere from 25°C to 900°C with a heating rate of 10°C min^{-1}. The X-ray diffraction (XRD) patterns of the mixed clays were recorded using Bruker AXS instrument equipped with Cu

Kα ($\lambda = 1.5406$ °A) radiation operating at 40 kV and 40 mA between 2θ in the range of 5 and 90° with a scan speed of $0.05° s^{-1}$. Nitrogen adsorption/desorption isotherms of the mixed clays were measured at −196°C by Beckmen-Coulter surface area analyzer (SA^{TM} 3100 model). Both the clay samples were degassed at 200°C for 2 h, prior to the N_2 adsorption/desorption analysis. The surface area was calculated using a multipoint Brunauer-Emmett-Teller (BET) model. The pore size distribution was obtained through the BJH model using the desorption isotherms and the total pore volume was estimated at a relative pressure of 0.99. FT-IR spectra were recorded between 4000 and 450 cm^{-1} region using Perkin-Elmer spectrometer (spectrum one model).

EXPERIMENTAL

Adsorption Isotherm Experiment

Calcined and uncalcined clays were used as an adsorbent for the adsorption of crystal violet dye. Batch equilibrium technique was followed for the adsorption isotherm studies. First, the dye was dried at 100°C for 2 h to remove the moisture. A stock solution of concentration, 2.45×10^{-3} M was prepared and the experimental solutions of the desired concentration were obtained by successive dilutions of the stock solution. For adsorption isotherm experiments, 50 ml of dye solution of known initial concentrations (in the range of 1.23×10^{-4} to 2.21×10^{-3} mol dm^{-3} for calcined mixed clay and 2.45×10^{-5} to 9.80×10^{-4} mol dm^{-3} for uncalcined mixed clay) were shaken with 0.05 g of adsorbent (calcined or uncalcined mixed clay) in an incubator shaker (Labtech®, Korea) at 150 rpm and at natural pH of the dye solution. The solution and solid phase were separated by centrifugation at 8000 rpm for 30 min in a high speed refrigerated table top centrifuge (Sigma Laborzentrifugen Gmbh, Model 4k15C). About 10 ml of the supernatant was collected without disturbing the centrifuged solution and analyzed spectrophotometrically (Perkin Elmer, Model Lamda 35) by measuring the maximum absorbance at the wavelength, λ_{max}, of 582 nm. In order to determine the thermodynamic parameters and to study the influence of temperature, the experiments were carried out at three different temperatures (30, 40, and 50°C). The amount of CV dye adsorbed at equilibrium was calculated by the following equation,

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

where, q_e is the amount of dye adsorbed at equilibrium (mol g^{-1}), V is the volume of the solution (dm^3), m is the mass of the adsorbent (g), C_0 and C_e are the initial and equilibrium concentrations of the dye, respectively, which is computed from the calibration curve.

Adsorption Kinetics Experiment

Kinetic adsorption experiments were conducted to find the effect of contact time of the adsorption process and to identify the adsorption rate. The kinetics of CV dye adsorption on calcined and uncalcined mixed clays were investigated at a fixed initial dye concentration (2.45×10^{-4} M) by adding 0.05 g of adsorbent into 50 ml of dye solution at pH of 4.20 (natural pH of CV solution). The mixture was shaken as a function of time in an incubator shaker at 150 rpm for three different temperatures (30, 40, and 50°C). At pre-determined time intervals, samples were taken and the concentration was measured. The amount of CV adsorbed q_t at time t was determined by the following equation,

$$q_t = \frac{V \times (C_0 - C_t)}{m} \tag{2}$$

where, q_t is the amount of dye adsorbed at time t (mol g^{-1}), V is the volume of the solution (dm^3), m is the mass of the adsorbent (g), C_0 and C_t are the concentrations of the dye at initial ($t = 0$) and at time t, respectively.

The effect of the adsorbent dosage on CV dye removal was studied by taking 0.01 to 0.2 g of calcined mixed clay and 0.02 to 0.8 g of uncalcined mixed clay for a fixed initial dye concentration of 2.45×10^{-4} M at 30°C (pH = 4.20). The influence of pH on dye removal was also carried out by performing the adsorption experiments by varying the dye solution pH from 2–10 for three different temperatures (30, 40, and 50°C) and the initial concentration of the dye solution was 2.45×10^{-4} M. The pH of the dye solution was adjusted by adding a few drops of NaOH or HCl to reach the desirable value, before shaking. All the adsorption experiments were always carried out in duplicate and the mean values were taken.

RESULTS AND DISCUSSIONS

Adsorbent Characterization

The TGA analysis of the clays used in the present work is shown in Fig. 1. The weight loss of kaolin, pyrophyllite, ball clay, and feldspar at 900°C is found to be 5, 5, 15, and 46%, respectively. However, quartz shows no weight loss during calcination. Generally the loss in weight is due to dehydration (100–220°C), dehydroxylation/decarbonation (220–600°C), and decomposition/phase transformation (600–900°C) (25). The loss of hydration water from pyrophyllite occurs below 200°C, while the weight loss due to dehydroxylation of the pyrophyllite begins about 500°C and the reaction is over at 825°C. The 5% weight loss of pyrophyllite is due to the release of structural OH (26). Commonly, kaolin-feldspar-quartz undergoes dehydroxylation at around 550°C and forms metakaolin ($Al_2O_3 \cdot 2SiO_2$). Metakaolin decomposes to mullite at high

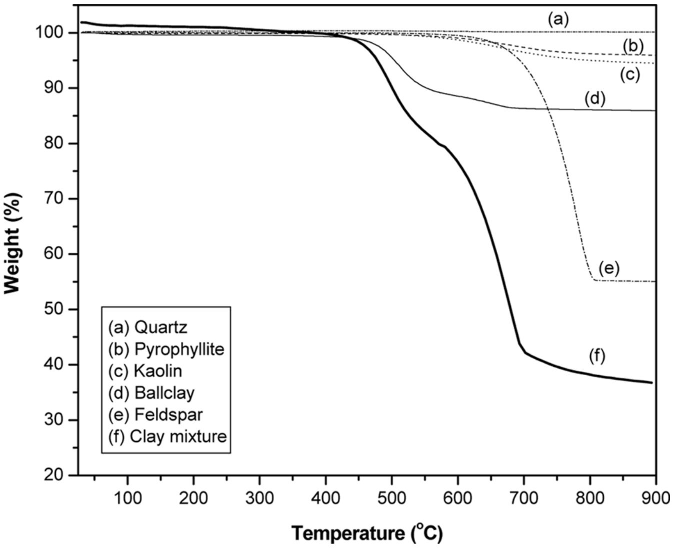


FIG. 1. Thermogravimetric curves of clays.

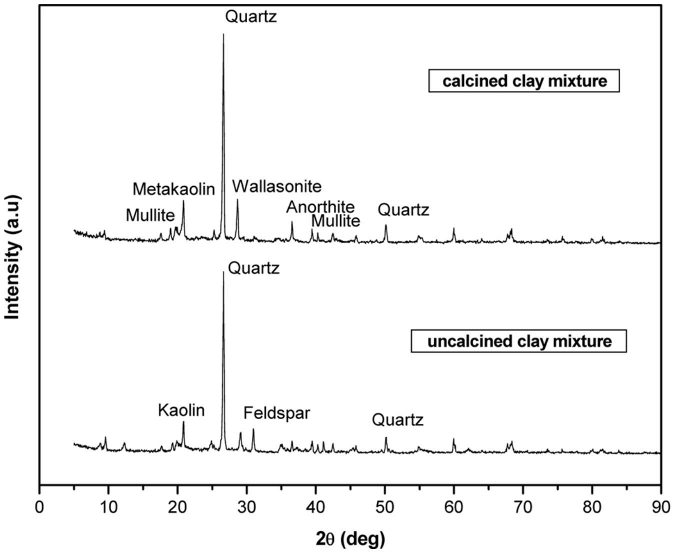


FIG. 2. XRD patterns of calcined and uncalcined mixed clay.

temperature (>850°C). The total weight loss of the mixed clay is found to be 64% during calcination between 25 and 900°C, which is mainly due to the reaction/phase transformation of the clays. During calcination, the destruction of layer arrangement occurs due to dehydration/dehydroxylation and also reorganization causes the opening of layers and generation of spaces (27). As the temperature increases, grains begin to melt and the liquid produced fills the space between the particles. This action decreases the pore volume of the calcined mixed clay. Calcination decreases the amount of hydroxyl groups which may affect the adsorption of dyes (28). In addition, the created hydrophobicity during calcination also makes the surface chemistry more compatible for organic systems.

Figure 2 depicts the XRD pattern of the calcined and uncalcined mixed clays. Generally, thermal transformation of clays undergoes a rearrangement of the existing structures that commonly occurs in preference to the complete disintegration followed by crystallization of a new phase. A series of reactions and phase transformations leads to the formation of new phases and disappearance of the others, which makes a shift in the peak position. After calcination, the major crystalline phase is found to be quartz and the various phases formed are also represented in Fig. 2. The intensity of all the reflections are decreased for the calcined mixed clay and the disappearance of all the reflections of kaolin peak indicate that the kaolin structure is entirely broken. The planes affected by defects due to dehydration increases the interlayer distances of the basal planes (29). The textural properties of the mixed clay (both calcined and uncalcined) are presented in Table 1. The crystallite size is calculated using Scherer's formula and found to be decreased during calcination.

$$d_{XRD} = \frac{K\lambda}{\beta \cdot \cos\theta} \tag{3}$$

where, d_{XRD} is the crystallite size (nm), K is the shape constant (0.9), λ is the wave length (1.5406 Å) of CuKα

TABLE 1
Textural properties of mixed clays

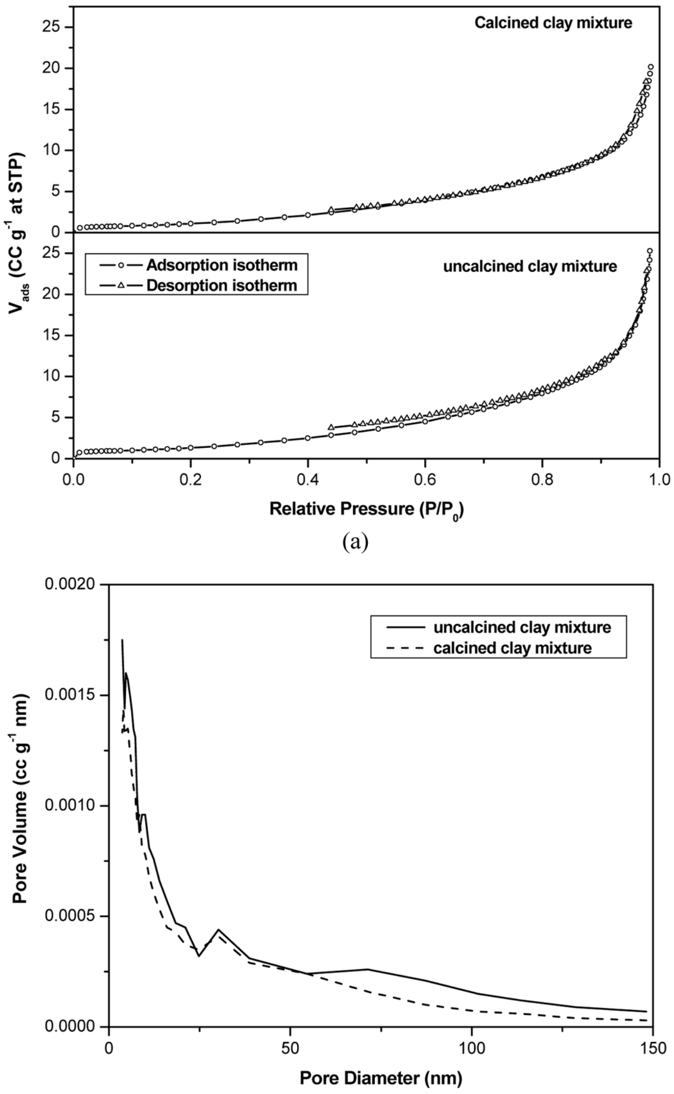
Sample	X-ray diffraction: Unit cell parameter [a] (nm)	X-ray diffraction: Crystallite size[b] (nm)	N_2 adsorption: S_{BET} (m^2g^{-1})	N_2 adsorption: V_{mes} ($ml\,g^{-1}$)	N_2 adsorption: Average pore diameter[c] (nm)
Calcined clay mixture	3.866	40.17	3.966	0.0283	28.54
Uncalcined clay mixture	3.866	41.51	4.771	0.0357	29.93

[a] Unit cell parameter $a_o = 2d_{100}/\sqrt{3}$. Where d_{100} is the d-spacing of (100) reflection.
[b] Crystallite size $d_{XRD} = \frac{K\lambda}{\beta \cdot \cos\theta}$. β is the full width at half maximum and λ is the wave length.
[c] Average pore diameter $D_p = 4\,V_{mes}/S_{BET}$. Where V_{mes} is the Mesopore volume and S_{BET} is the BET surface area.

radiation, β is the full width at half maximum, and θ is the diffraction angle (degrees).

The nitrogen adsorption/desorption isotherms and pore size distribution of the calcined and uncalcined mixed clays are shown in Figs. 3a and 3b. The uncalcined mixed clay shows a nonporous Type-II isotherm and also shows a hysteresis loop arising from the presence of mesopores. As can be seen from the Table 1, the BET surface area of the calcined mixed clay is found to be $3.966\,m^2\,g^{-1}$ ($4.771\,m^2\,g^{-1}$ for uncalcined mixed clay) with pore volume of $0.0283\,ml\,g^{-1}$ ($0.0357\,ml\,g^{-1}$ for uncalcined mixed clay). The surface area and pore volume of the mixed clays are decreased during calcination, which may be due to the formation of the agglomerate structures by partial fusion of particles producing higher amount of coarse fractions (30).

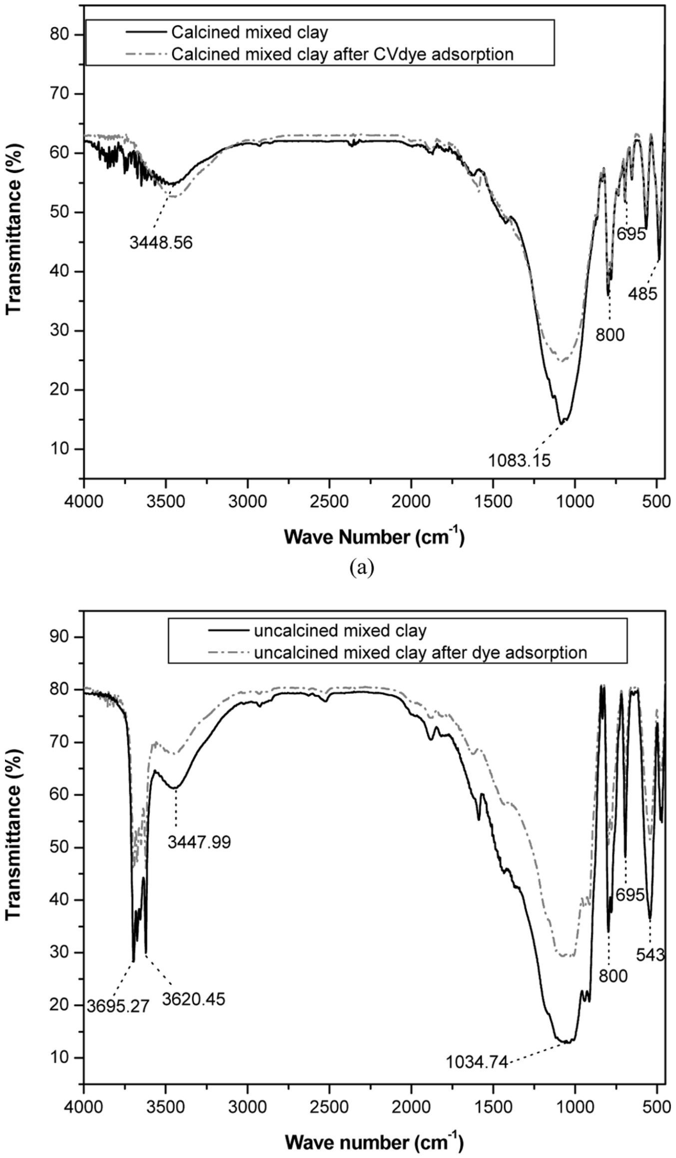
FTIR spectrum of the calcined and uncalcined mixed clays is shown in Figs. 4a and 4b. The bands at 3620 and $3695\,cm^{-1}$ corresponds to the adsorbed water and the band at $3447\,cm^{-1}$ correspond to the O-H stretching of the silica group present in the mixed clay. The OH bending band appears at $985\,cm^{-1}$ for the uncalcined mixed clay. The asymmetric stretching vibration of Si–O–Si of the SiO_4 tetrahedron is observed at 695, 800, and $1035\,cm^{-1}$ (due to the presence of quartz) (26). The absorption peaks around 460 to $700\,cm^{-1}$ are mainly due to bending



(a)

(b)

FIG. 3. (a) N_2 adsorption/desorption and (b) pore size distribution of calcined and uncalcined mixed clays.



(a)

(b)

FIG. 4. FTIR Spectra of (a) calcined and (b) uncalcined mixed clays before and after dye adsorption.

vibration of Si–O–Si bonds and the band at 467 cm^{-1} corresponds to Si–O bond. During calcination, the bands corresponds to hydroxyl group at 3695 and 3620 cm^{-1} are vanished completely due to the removal of adsorbed water present in the uncalcined mixed clays(22). The removal of adsorbed water and decrease in the intensity of SiO–H stretching band (3447 cm^{-1}) indicates the reduction of surface hydroxyl group, which will have a detrimental effect on adsorption of dyes.

Adsorption Isotherm

Generally, the adsorption isotherms with a specific adsorbate are carried out to estimate the adsorption characteristics. A concentration variation method is used to calculate the adsorption characteristic of the adsorbent and the process. Equilibrium isotherms are very important in the design of any adsorption processes. The adsorption equilibrium studies of CV on calcined and uncalcined mixed clays were carried out at 30, 40, and 50°C and fitted with the Langmuir and Freundlich isotherm models. The models are fitted in nonlinear form without linearization as we know that the linearization leads to an error value of correlation coefficients (R^2) depending on in which form it is linearized. So it is difficult to predict the actual isotherm. Nonlinear method is the best way to get the actual isotherm parameters (31). The homogeneous Langmuir adsorption isotherm (32) is represented by the following equation,

$$q_e = \frac{Q_{max} K_L C_e}{(1 + K_L C_e)} \tag{4}$$

where, q_e is the adsorbed amount of the dye at equilibrium (mol g^{-1}), C_e is the equilibrium concentration of the dye in solution (mol dm^{-3}), Q_{max} is the maximum adsorption capacity (mol g^{-1}), and K_L is the constant related to the free energy of adsorption (dm^3 mol^{-1}).

The heterogeneous Freundlich adsorption isotherm (33) is represented by the following equation,

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

where, K_F is the Freundlich isotherm constant (mol g^{-1} (dm^3 mol^{-1})$^{1/n}$) and 1/n is the adsorption intensity (dimensionless).

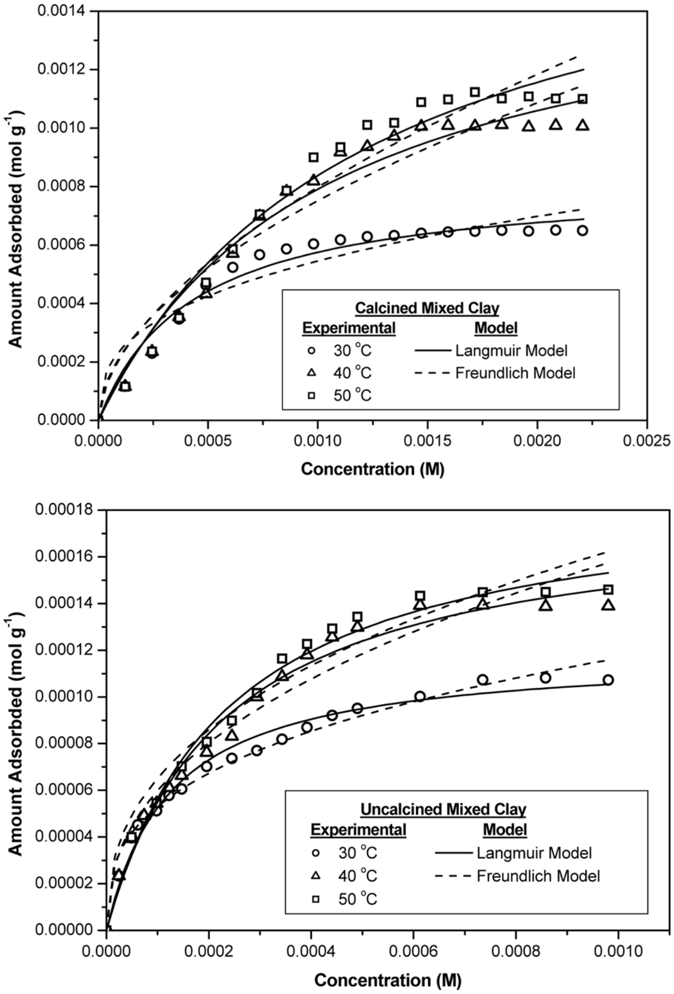


FIG. 5. Adsorption isotherm models of CV on calcined and uncalcined mixed clays at different temperatures.

Figure 5 shows the Langmuir and Freundlich isotherm models fitted with the obtained experimental data and the model parameters are listed in Table 2. The reported adsorption data were obtained by a dye concentration measurement after the adsorbent/adsorbate contact time equal to the equilibrium times. It is observed from Table 2 that the uptake of CV by both the mixed clays (calcined and uncalcined) increases with an increase in the temperature indicates higher interaction energies between CV dye and adsorbents. Similar results have been reported for the adsorption of reactive red MF-3B onto organo-clay (10) and reactive dye onto chemically cross-linked chitosan blends (34). The maximum adsorption capacity of the calcined and uncalcined mixed clay is found to be 1.9×10^{-3} and 1.9×10^{-4} mol g^{-1}, respectively at 50°C. The high adsorption capacity of the calcined mixed clay over the uncalcined mixed clay may be attributed to the different mechanism (explained later in the proposed mechanism section). The correlation coefficients (R^2) of both the models are compared and a greater correlation coefficients value is obtained for the Langmuir model at all temperatures indicates that the Langmuir model could better describe the adsorption of CV on both calcined and uncalcined mixed clays. Generally, the hydrophilic sites of the clays are responsible for the adsorption of polar organic molecules and the hydrophobic sites are responsible for the adsorption of nonpolar molecules. Although

TABLE 2
Parameters of adsorption isotherms of CV on calcined and uncalcined mixed clay at different temperatures

		Langmuir isotherm			Freundlich isotherm		
Adsorbent	Temperature (°C)	Q_{max} (mol g^{-1})	K_L (dm^3 mol^{-1})	R^2	K_F (mol g $^{-1}$ (dm^3 mol^{-1})$^{1/n}$)	1/n	R^2
Calcined clay mixture	30	8.2×10^{-4}	2.332×10^3	0.969	6.37×10^{-3}	0.356	0.892
	40	1.6×10^{-3}	0.97×10^3	0.971	2.96×10^{-2}	0.531	0.912
	50	1.9×10^{-3}	0.814×10^3	0.976	4.07×10^{-2}	0.569	0.904
Uncalcined clay mixture	30	1.2×10^{-4}	7.962×10^3	0.982	1.23×10^{-3}	0.342	0.896
	40	1.8×10^{-4}	4.403×10^3	0.984	2.96×10^{-3}	0.423	0.921
	50	1.9×10^{-4}	4.245×10^3	0.987	2.59×10^{-3}	0.400	0.909

the surface of the clays are structurally heterogeneous in nature, the active adsorption sites for the polar dye molecules are hydrophilic edge surfaces suggesting that the surface is energetically homogeneous with respect to adsorption energy. The dye molecules may chemically adsorb on the edge of the crystal, which forms a binding with the tetrahedrally and octahedrally coordinated Lewis base sites that are previously hydrated with hydroxyls of the water molecules (17). The maximum adsorption capacity of CV in the present study is compared with other adsorbents reported in the literatures (Table 3). It is very clear that the adsorption capacity of calcined mixed clay is much higher than that of the other potential adsorbents such as polygorskite, sepiolite (raw and modified), kaolinite, bentonite (raw and modified), and charred saw dust. Thus based on the results obtained (Table 3), both the mixed clays (calcined and uncalcined) could be employed as low cost adsorbents for an alternative to commercial activated carbons and other individual clays for the removal of colors.

TABLE 3
Reported maximum adsorption capacity of CV dyes on various adsorbents

Adsorbent	Adsorption capacity (mol g^{-1})	Ref.
Palygorskite	1.42×10^{-4}	9
Raw sepiolite	1.80×10^{-4}	19
Base activated sepiolite	4.10×10^{-4}	19
Raw bentonite	3.50×10^{-4}	20
Co-saturated bentonite	5.6×10^{-4}	20
Kaolin	1.16×10^{-4}	35
CDBA-bentonite	8.80×10^{-4}	36
CP-bentonite	1.02×10^{-3}	36
Activated carbon produced from sewage sludge	1.67×10^{-4}	37
Charred saw dust	9.29×10^{-4}	38
Calcined mixed clay	1.90×10^{-3}	Present work
Uncalcined mixed clay	1.90×10^{-4}	Present work

Thermodynamic Parameters

The thermodynamic parameters of CV adsorption on both the calcined and uncalcined mixed clays are determined, since both energy and entropy are the key factors to be considered in any process design. The Gibbs free energy change for the adsorption process is expressed by the following equation,

$$\Delta G^0 = -RT \ln K \tag{6}$$

where, ΔG^0 is the change in free energy (kJ mol^{-1}) and R is the gas constant (8.314 J mol^{-1} K^{-1}). The change in enthalpy and entropy are related to the Gibbs free energy and are calculated based on the adsorption isotherms by the following equations,

$$\Delta H^0 = -R\left(\frac{T_2 T_1}{T_2 - T_1}\right) \ln \frac{K_1}{K_2} \tag{7}$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \tag{8}$$

where, ΔH^0 is the change in enthalpy (kJ mol^{-1}), ΔS^0 is the change in entropy (kJ mol^{-1} K^{-1}), T is the absolute temperature (K), K_1 and K_2 are the Langmuir constants at $T_1 = 30$°C and $T_2 = 50$°C, respectively. The thermodynamic parameters for the adsorption of CV on calcined and uncalcined mixed clay are given in Table 4. The negative values of ΔG^0 at different temperatures indicate that the adsorption of CV on both the adsorbents are thermodynamically feasible and spontaneous in nature. In general, ΔH^0 value in the range of −5 to −40 kJ mol^{-1} corresponds to physisorption mechanism and in the range of −40 to −800 kJ mol^{-1} suggests a chemisorption mechanism (5). However, the dividing line between the physical

TABLE 4
Thermodynamic parameters for the adsorption of CV on calcined and uncalcined mixed clay

	ΔG^0 (KJ mol^{-1})				
Adsorbent	30°C	40°C	50°C	ΔH^0 (KJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
Calcined clay mixture	−19.54	−17.90	−18.00	−42.82	−76.83
Uncalcined clay mixture	−22.63	−21.84	−22.43	−25.59	−9.77

and chemical adsorption is not sharp (5). In this work, the ΔH^0 values are found to be −42.82 and −25.59 kJ mol^{-1} for calcined and uncalcined mixed clays, respectively, which indicates that the adsorption mechanism is physical adsorption for calcined and uncalcined mixed clays. However, the higher negative ΔH^0 value for calcined mixed clays indicates that the physical interaction between the calcined mixed clay and the dye molecules are very strong than that of uncalcined mixed clay. The negative ΔS^0 values indicate the decreased randomness at the solid/solution interface (38).

Proposed Adsorption Mechanism

In general, the exchangeable cations tend to diffuse into the bulk water when clays are mixed with water. As this diffusion process proceeds it creates repulsion forces between the clay platelets that leads to the dispersion of the clay in water. The degree of dispersion depends on the nature of the clay, interlayer cation, and surface charges. The dispersions of clay minerals contain layered particles or their crystallites composed of many layers (14). The individual layers of clay contain a negative surface charge owing to the presence of variable and permanent charges. The variable charge occurs at the layer edges of clay, dominantly at hydroxyl groups, and exhibits acid/base properties. These permanent charges of clays are due to the presence of the central atoms within the octahedral and/or tetrahedral sheets (39).

Cationic dyes always have strong affinity for the clay surfaces, as a result of electrostatic attractions as well as other effects such as the very high hydrophobicity of these molecules (14). So the adsorption capacity is high in both calcined (1.9×10^{-3} mol g^{-1}) and uncalcined (1.9×10^{-4} mol g^{-1}) mixed clays, in spite of the low surface area and pore volume. However, uncalcined mixed clay is nonexpandable in water, which restricts its dispersion in water and the intercalation of organic molecules in the interlamellar spaces. This incomplete dispersion leads to the formation of microaggregates called tactoids. So the interaction of dyes takes place at the tactiod edges as well as on the O-atom sheet at the interlamellar space. However, dyes with nonplanar structures like CV will find more difficulty to enter into this region due to shorter interbasal distances between the layers (14). Due to this reason the adsorption capacity of uncalcined mixed clays are lower than the calcined mixed clays. After dye adsorption, there is a shift in the FT-IR band position (see Fig. 4b). The decrease in the intensity of siloxane band (−Si−O−Si−) at 1035 cm^{-1}, silanol band (SiO−H) at 3447 cm^{-1} and the hydroxyl bands due to adsorbed water at 3620 and 3695 cm^{-1} is observed for uncalcined mixed clays indicates that the sites are occupied by the dye molecules.

In calcined mixed clays, the disappearance of the OH groups, which is originally found in uncalcined mixed clays, will reduce the adsorption capacity of the calcined clays due to reduction in the active sites. It is clear from Table 1 that the surface area and pore volume are decreased for calcined mixed clays. However, a drastic increase in the obtained adsorption capacity (Table 2) could not be properly explained using surface area and pore volume concept. So, the adsorption of CV dye on calcined mixed clay follows a different mechanism. During calcination, the dehydration takes place which creates defects in the planes leads to increase the interbasal spacing (29). When the calcined clay is mixed with water, it expands and forms platelets due to the increase in the interbasal distance between layers. The expansion of these layers may leads to the bilayer coverage of the dyes i.e., two layers of CV cations lying flat in the interlayer space (39,40). The adsorbed dyes on the outer surface migrate towards the inner interlamellar regions could cause an increase in the adsorption of the dye molecules. It seems from the Fig. 4a, that the intensity of the band (3442 cm^{-1}) corresponds to the surface hydroxyl group is increased after dye adsorption. Generally, the surface hydroxyl group would decrease after dye adsorption, however an increase in the hydroxyl group after dye adsorption is observed for calcined mixed clays due to the water molecules entering into the interlayer creating more hydroxyl groups that can be utilized by the dye molecules during adsorption. So the increase in the basal spacing and the formation of a multilayer during calcination plays a vital role and causes drastic increase in the adsorption capacity of the CV dye molecule on calcined mixed clays (29).

Effect of Adsorbent Dosage

The effect of the adsorbent (calcined and uncalcined mixed clay) dosage for CV dye adsorption is shown in

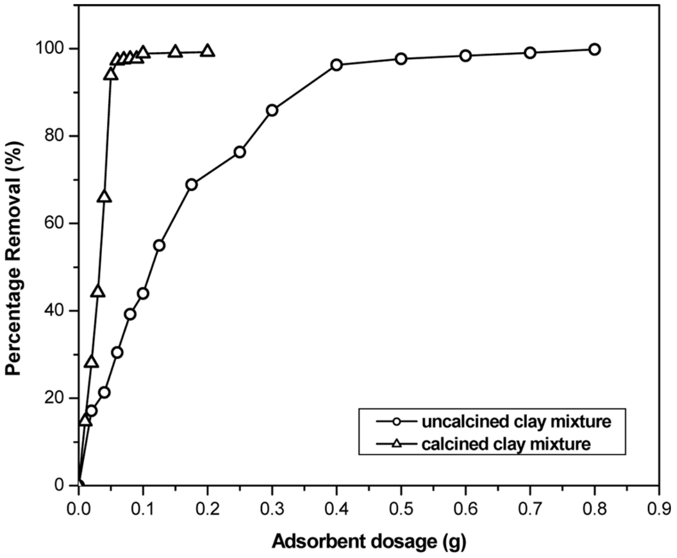


FIG. 6. Dosage effect of calcined and uncalcined mixed clays for crystal violet dye adsorption.

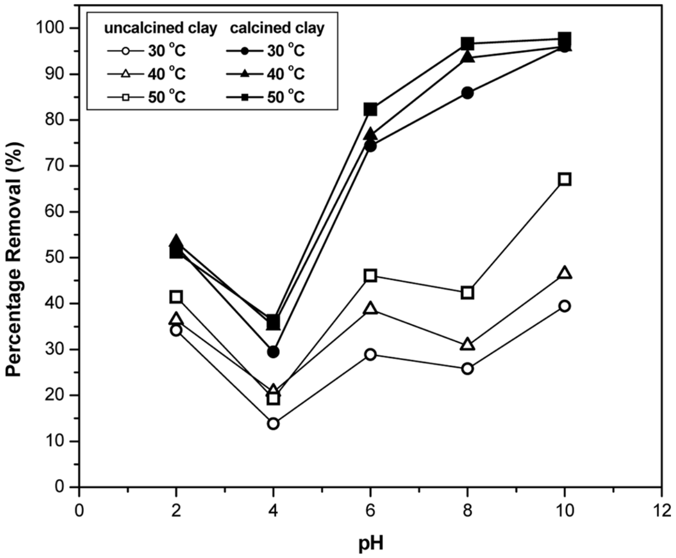


FIG. 7. Influence of pH on adsorption of CV on calcined and uncalcined mixed clays at different temperatures.

Fig. 6. The percentage of dye removal increases with increase in the mass of the adsorbent dosage which is due to the increase in the number of active sites for CV dye adsorption and a complete removal of dye solution is observed at a particular mass of both the adsorbent. For uncalcined mixed clay, only 25% of CV is removed by 0.05 g mass of the adsorbent and 0.8 g is required for complete removal. In the case of calcined mixed clay, 94% removal of CV requires 0.05 g of the adsorbent and only 0.2 g is needed for the complete removal of CV dye. The amount of dye adsorbed per unit mass of the adsorbent is decreased from 1.05×10^{-4} to 1.53×10^{-5} mol g^{-1} for the uncalcined mixed clay of 0.02 to 0.8 g. However, for calcined mixed clay, the amount of dye adsorbed per unit mass of the adsorbent is increased from 1.80×10^{-4} to 2.30×10^{-4} mol g^{-1} for the adsorbent mass of 0.01 to 0.05 g and then it decreases to 6.08×10^{-5} mol g^{-1} for 0.2 g of adsorbent mass.

Effect of pH

The pH of the dye solution is an important controlling parameter in adsorption because it affects the surface charge of the adsorbent, the degree of ionization of the materials present in the solution, the structural stability, and the color intensity of the dye molecule. The hydrogen and hydroxyl ions are adsorbed quite strongly and therefore, the adsorption of other ions is affected by the pH of the solution. The influence of pH on the dye adsorption on calcined and uncalcined mixed clays was studied for 50 ml of dye solution of initial concentration of 2.45×10^{-4} M by adding 0.05 g of adsorbent (calcined and uncalcined mixed clay). The percentage removal of CV over the pH ranges of 2 to 10 is shown in Fig. 7. The percentage removal of CV on calcined mixed clays increases with increasing the pH from 4 to 10 and a maximum removal of 98% is obtained at pH 10. As the pH increases, the number of negative sites on the surface of the clay particles also increases. Therefore, an increase in the adsorption of the CV dye on the clays is observed at higher pH due to the presence of excess hydroxyl group. It is also explained by other ways that the increase in the pH of the solution decreases the charge density, which increases the electrostatic attraction between the positively charged dye and the negatively charged adsorbent surface results in an increase in the extent of the adsorption of CV. The minimum removal of CV is found at pH 4 that is probably due to the presence of excess H^+ ions competing with the cation groups on the dye for adsorption sites. The higher rate of CV removal at pH 2 is due to the dissociation of the dye molecules. The pH trend for the uncalcined mixed clay follows the same trend as like calcined mixed clay; however, the maximum percentage removal of color is lower (68%) than the calcined mixed clay at pH 10 for the same initial concentration. However, there is a decrease in the percentage color removal at pH 8. Eren and Afsin (20) have also reported similar observations for the adsorption of CV. Based on the result, it is clear that the adsorption process is highly dependent on the pH of the solution.

Kinetic Study

The kinetic study of the adsorption process provides useful information regarding the efficiency of adsorption and feasibility of scale-up operations. It also provides the

TABLE 5
Parameters of kinetic models of CV adsorption on calcined and uncalcined mixed clay at different temperatures

			Pseudo first order model			Pseudo second order model		
Adsorbent	Temperature (°C)	$q_{e,exp}$ (mol g^{-1})	k_1 (min^{-1})	$q_{e,cal}$ (mol g^{-1})	R^2	k_2 (g mol^{-1} min^{-1})	q_e (mol g^{-1})	R^2
Calcined mixed clay	30	2.30×10^{-4}	0.265	2.24×10^{-4}	0.996	4.40×10^{3}	2.30×10^{-4}	0.999
	40	2.35×10^{-4}	0.267	2.27×10^{-4}	0.994	4.44×10^{3}	2.36×10^{-4}	0.999
	50	2.36×10^{-4}	0.291	2.28×10^{-4}	0.994	5.62×10^{3}	2.36×10^{-4}	0.999
Uncalcined mixed clay	30	7.36×10^{-5}	0.138	6.00×10^{-5}	0.946	2.32×10^{3}	6.59×10^{-5}	0.999
	40	8.31×10^{-5}	0.076	7.87×10^{-5}	0.929	1.60×10^{3}	8.46×10^{-5}	0.999
	50	8.98×10^{-5}	0.068	8.28×10^{-5}	0.912	1.21×10^{3}	9.03×10^{-5}	0.999

information about the factors affecting the reaction rate and explains how fast or slow the chemical reaction occurs which should be very useful in the selection of the adsorbent material. Numerous kinetic models have described the reaction order of adsorption systems based on the solution concentration and the capacity of the adsorbent. In this work, the kinetic data of CV adsorption on calcined and uncalcined mixed clays is evaluated using the most widely used pseudo-first-order kinetic model (41) and pseudo-second-order kinetic model (42), which is expressed by the following equations;

$$q_t = q_e(1 - e^{-k_1 t}) \tag{9}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{10}$$

where, k_1 is the pseudo-first-order rate constant (min^{-1}), k_2 is the equilibrium rate constant of pseudo-second-order adsorption mechanism (g mol^{-1} min^{-1}), q_e and q_t are the amount of dye adsorbed at equilibrium (mol g^{-1}) and at time t (mol g^{-1}), respectively.

The adsorption kinetics of CV on calcined and uncalcined mixed clay is fitted with both the kinetic models (Figure not shown here) and the results are presented in Table 5. It is observed from Table 5 that the calculated values of q_e from the pseudo-second order model shows good agreement with the experimental q_e values for the temperatures studied. In addition, the regression coefficient of second-order kinetics is greater than the first-order kinetics for the adsorption of CV dye on both the mixed clays. It suggests that the adsorption follows a second-order rate equation.

CONCLUSIONS

In this work, we have successfully demonstrated the applicability of locally available and cheaper mixed clays (calcined and uncalcined) as a potential adsorbent for the removal of crystal violet from aqueous solution. The TGA and XRD analysis reveals that the mixed clay undergoes various reactions/phase transformations during calcination resulting in a weight loss of 64%. The sharp peak of XRD indicates that both the calcined and uncalcined mixed clays are crystalline and the formation of new phases like mullite increases the interbasal spacing which favors adsorption. It is observed that the surface area and the pore volume of the calcined mixed clay decrease during calcination. The equilibrium isotherm study indicates that the adsorption capacity increases with an increase in the temperature for both the mixed clays. Calcined mixed clay shows an extremely high adsorption capacity of 1.9×10^{-3} mol g^{-1}, which is one order greater than that of the uncalcined mixed clay. The reason for the higher adsorption capacity of the calcined clay is the increase in the interbasal spacing and hydroxyl group due to expansion of the layers of clays when it mixed with water. The Langmuir model is found to be the best fit for the adsorption of CV on both the mixed clays compared to the Freundlich model. The removal efficiency of CV increases with increasing the pH from 4 to 10 for both the adsorbent. Thermodynamic parameters indicate that CV adsorption on both the mixed clays is spontaneous and endothermic in nature. The percentage removal of CV increases with an increase in the dosage for both the adsorbents indicating the increase in the adsorption sites. The results obtained from the kinetic study confirm that the adsorption of CV follows the pseudo-second order rate equation. Based on the higher adsorption capacity of these mixed clays (calcined and uncalcined), it is concluded that these materials could be used as an alternative adsorbent to the expensive activated carbon for the removal of colors from aqueous solution.

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