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Utilization of ball clay adsorbents for the removal of crystal violet dye from aqueous solution

P. Monash · Ram Niwas · G. Pugazhenthi

Abstract In this work, an attempt has been made to find the adsorption characteristics of crystal violet (CV) dye on calcined and uncalcined ball clay using batch adsorption technique. The ball clay adsorbents are characterized using thermo gravimetric analysis (TGA), particle size analysis, X-ray diffraction (XRD), nitrogen adsorption–desorption isotherm, and Fourier transform infrared (FT-IR) spectroscopy. The influence of pH and temperature on the adsorption of CV dye is examined. The experimental results of adsorption isotherms are fitted with Langmuir, Freundlich, and Redlich–Perterson models. Adsorption mechanisms of the CV dye on both the ball clays are investigated using thermodynamic parameters and analytical techniques. The results indicate that the Langmuir and Redlich–Peterson models are found to be the more appropriate model to explain the adsorption of CV dye on ball clays than that of Freundlich model. The maximum adsorption capacity of the calcined and uncalcined ball clay is found to be 1.6×10^{-4} and 1.9×10^{-4} mol g^{-1}, respectively. The lower adsorption capacity of the calcined ball clay is due to the reduction in the surface hydroxyl group and surface area. Adsorption capacity and percentage removal of the CV dye on calcined and uncalcined ball clay increase with an increase in the temperature and pH, respectively. The obtained negative ΔG^0 values indicate that the adsorption of CV dye on ball clay is feasible and spontaneous in nature at temperatures studied. The energy supplied for calcining the ball clay did not bring any improvement in the adsorption capacity. Rather, a reduction in the adsorption capacity of the CV dye on calcined ball clay suggests that the uncalcined ball clay would be more economic and efficient adsorbent for the removal of CV dye than the calcined ball clay. In conclusion, uncalcined ball clay could be used as a low cost alternate for the expensive activated carbon.

Variables

C_0	Initial concentration (mol dm^{-3})
C_e	Concentration at equilibrium (mol dm^{-3})
CAL BC	Calcined ball clay
CV	Crystal violet
ΔG^0	Change in Gibbs free energy (KJ mol^{-1})
ΔH^0	Change in enthalpy (KJ mol^{-1})
K_F	Freundlich constant (mol g^{-1} (l mol^{-1})$^{1/n}$)
K_L	Langmuir constant (l mol^{-1})
K_{RP}	Redlich–Peterson constant (mol g^{-1})
m	Mass of the adsorbent (g)
n	Adsorption intensity (dimensionless)
q_e	Dye adsorbed amount at equilibrium (mol g^{-1})
Q_{max}	Maximum adsorption capacity (mol g^{-1})
ΔS^0	Change in entropy (KJ mol^{-1} K^{-1})
UNCAL BC	Uncalcined ball clay
V	Volume (l)

Greeks

θ	Angle of diffraction (degrees)
λ_{max}	Maximum absorbance wavelength (nm)

P. Monash · G. Pugazhenthi (✉)
Department of Chemical Engineering, Indian Institute
of Technology Guwahati, Guwahati 781039, Assam, India
e-mail: pugal@iitg.ac.in

R. Niwas
Department of Chemical Engineering, National Institute
of Technology, Tiruchirappalli 620015, Tamilnadu, India

Introduction

Synthetic dyes are widely used in textile, paper, carpet, printing, and leather industries and produces huge volumes of dye wastewater (Hu et al. 2007). Nowadays, due to the stringent environment regulations, most industries use efficient and clean technologies for the treatment of the hazardous dye wastewater to avoid any serious problems to human being and aquatic lives (Hu et al. 2007; Weng and Pan 2007). Cationic crystal violet (CV) dye is most widely used as a biological stain, dermatological agent and in medicine (Adak et al. 2005; Eren and Afsin 2007; Rytwo et al. 2007). However, CV is toxic to mammalian cells and also a mutagen and mitotic poison (He et al. 2010). Textile and paper printing industries also produce large amount of wastewater containing CV dye that must be treated to reduce its impact on environment (Adak et al. 2005; Senthilkumaar et al. 2006a, b; Eren and Afsin 2007; Rytwo et al. 2007). Various treatment methods have been developed for the treatment of the dye wastewater and adsorption has been recognized to be one of the promising and cost effective processes for treating dye wastewater (Adak et al. 2005; Weng and Pan 2007). Although, many kinds of adsorbents have been developed, activated carbon is a more effective and versatile adsorbent for the treatment of dye wastewater (Garg et al. 2004; Crini 2006; Zohra et al. 2008). However, high cost and difficulty in regeneration of the activated carbon (Chakraborty et al. 2005; Gurses et al. 2004; Al-Futaisi et al. 2007; Eren and Afsin 2007) drive the researchers in search for low cost materials having reasonable adsorptive efficiency as substitutes for the expensive activated carbon (Crini 2006; Gurses et al. 2004; Zohra et al. 2008; Gupta and Suhas 2009). Many low cost adsorbents such as wood (Kannan and Sundaram 2001), sawdust (Chakraborty et al. 2005), rice husk (Malik 2003), bagasse (Juang et al. 2002; Mall et al. 2006), peels of banana and orange (Namasivayam et al. 1996; Annadurai et al. 2002), peanut hulls (Gong et al. 2005), peat (Sun and Yang 2003), fullers earth (Atun et al. 2003), flyash (Mohan et al. 2002) etc., were investigated for the treatment of dye wastewater. The adsorption capacity of the low cost adsorbents for different types of dyes was reported elsewhere (Garg et al. 2004; Crini 2006; Gupta and Suhas 2009).

Many research works has focused on the utilization of low cost clays for the adsorption of dyes to bring massive economic and environmental benefits. Clays have advantages over other commercial adsorbents in terms of low cost, high adsorption capacity, non-toxicity, and large potential for ion exchange, resulting from a net negative charge on the structure of the minerals (Alkan et al., 2007; Vimonses et al. 2009a, b). Many investigations have been carried out for the adsorption of CV dye on different types of clay such as bentonite (Eren and Afsin 2008), kaolinite (Nandi et al. 2008), montmorillonite (Yariv et al. 1989; Rytwo and Gonen 2006), palygorskite (Al-Futaisi et al. 2007), perlite (Dogan and Alkan 2003), pillared clay (Mishael et al., 1999; Vindod and Anirudhan 2003), and sepiolite (Eren and Afsin 2007).

Rytwo et al. (1995) studied the interactions between cationic CV dye and montmorillonite. They found an improved adsorption capacity when the concentration of CV was higher than the cation exchange capacity of montmorillonite. Ghosh and Bhattacharyya (2002) investigated the adsorption of methylene blue dye on local kaolin of six different forms (raw, pure, calcined raw, calcined pure, NaOH treated raw and NaOH treated pure kaolin). They reported that the raw kaolin showed a higher adsorption capacity than calcined kaolin. When treated with NaOH, kaolin had enhanced adsorption capacity for cationic dye. Dogan and Alkan (2003) investigated the adsorption of CV dye on perlite and found that the adsorption capacity of the unexpanded perlite was higher than the expanded perlite. They suggested that the decrease in the adsorption capacity of the expanded perlite was due to the reduction in the hydroxyl group and micropores during calcination. Al-Futaisi et al. (2007) have examined CV dye adsorption capacity of palygorskite using distilled water and real groundwater. Their investigation revealed that the adsorption of dyes onto palygorskite was found to be more effective in ground water than the distilled water. The salts present in the ground water enhanced the adsorption of dyes onto palygorskite. However, the fine fractions of palygorskite obtained by washing (to remove the carbonates, soluble salts, organic matters) of the palygorskite clay did not show any enhancement in the adsorption capacity compared to that of the raw palygorskite. Eren and Afsin (2007, 2008) have studied the adsorption of CV dye on various forms of sepiolite and bentonite surfaces. They concluded that the permanent charges present in the basal surface have a lot of influence on the adsorption capacity. Nandi et al. (2008) looked at the effect of temperature, pH, adsorbent dosage, agitation speed and contact time for the adsorption of CV dye on pure kaolin. They reported that the adsorption of CV dye was highest at zero point charge of the adsorbent. In our previous work (Monash and Pugazhenthi 2010), the adsorption of CV dye on calcined and uncalcined mixed clay adsorbents was investigated and the adsorption capacity of the calcined mixed clay was one order higher than the uncalcined mixed clay. The above cited work reveals that the adsorption of CV dyes on clays depends on various parameters and the interaction between the dye molecule and the adsorbent.

In general, clays are in the form of flat hexagonal plates and based on the orientation, the plates will form two different types of structures, viz. card stack or card house (Frank and Hamer 2004). The adsorption capacity of the dyes will vary based on the orientation and the surface

charge (Yariv and Cross 2002; Somasundaran and Hubbard 2006). Increase or decrease in the adsorption of dyes onto clays mainly depends on the dispersion of clays in water, surface area, structure, and surface chemistry of the clays (Somasundaran and Hubbard 2006). Information on the above parameters is necessary to predict the possible interactions between the clay and the dye molecules. In addition to that, some isomorphic substitutions also takes place in the tetrahedral sheet of the lattice leading to negatively charged adsorption sites which are occupied by exchangeable cations. The surface charge originates from isomorphic substitutions for Si^{4+} or Al^{3+} by lower valency ions inside the crystal and creates a charge deficiency (Somasundaran and Hubbard 2006). These points are chemically active positions and play a vital role in the adsorption processes.

Kaolin has received considerable attention as an adsorbent because of its high adsorption capacity (Ghosh and Bhattacharyya 2002; Nandi et al. 2008; Vimonses et al. 2009a, b). Ball clay is a variety of kaolin containing 60–80% of kaolin and small quantities of quartz and other impurities (Yariv and Cross 2002; Ciullo 1996). For the removal of dyes, ball clay might be used as a low cost adsorbent instead of expensive activated carbon. There are some updated works on the adsorption of heavy metals onto ball clay (Holdridge 1969; Chantawong et al. 2003). However, few or no literatures have been found on the adsorption of CV dye onto ball clay.

The objective of the present study is to assess the ability of low cost ball clay (calcined and uncalcined) for the removal of CV dye from aqueous solution. The adsorbent, ball clay, is characterized with thermo gravimetric analysis (TGA), particle size analysis, X-ray diffraction (XRD), nitrogen adsorption–desorption isotherms, and Fourier transform infrared (FT-IR) spectroscopy. The adsorption mechanism of CV dye on calcined and uncalcined ball clay is investigated using batch equilibrium adsorption isotherm experiments carried out at 30, 40, and 50°C. The experimental equilibrium adsorption data are fitted with Langmuir, Freundlich, and Redlich–Peterson isotherm models to extract the isotherm parameters. The influence of pH on adsorption is also investigated over the pH ranges between 2 and 11. In addition, the thermodynamic parameters are predicted using the isotherm data to get an insight of the adsorption mechanism of CV dye on ball clay.

Materials and methods

Materials

Raw ball clay used in this work was collected from Kanpur (India). CV (C.I. 42555, chemical formula = $C_{25}H_{30}N_3Cl$,

Mol. Wt. = 407.99, Loba Chemie, Mumbai, India). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) (Merck (I) Ltd, Mumbai, India) were used as received. Millipore (model: Elix 3 make: Millipore) water was used for the preparation of dye solution.

Methods

Preparation of the adsorbents

Hundred grams of air dried raw ball clay was sieved in a 200-mesh standard sieve and the undersize was stirred with Millipore water in a Borosil beaker for 3 h. Then the mixture was kept undisturbed for 60 min and the soluble impurities were removed (Al-Futaisi et al. 2007). The above process was repeated several times by adding Millipore water. Finally, the ball clay was dried in a hot air oven at 120°C. The dried ball clay was separated into two halves. The first half (dried at 120°C) was named as uncalcined ball clay (UNCAL BC) and the second half was calcined at 900°C for 6 h and it was named as calcined ball clay (CAL BC). The prepared adsorbents were stored in an air tight bottle and used for the adsorption of CV dye from aqueous solution.

Characterization methods

The adsorbents (CAL BC and UNCAL BC) were characterized using TGA, XRD, N_2 adsorption/desorption, particle size analysis and FT-IR spectroscopy. TGA was performed on the Mettler Toledo thermo gravimetric analyzer (TGA/SDTA 851® model) under air atmosphere from 25 to 900°C with a heating rate of 10°C min^{-1}. The particle size distribution analysis of the clays was carried out in a particle sizing machine, Malvern Mastersizer 2000 (APA 5005® model, hydro MU) in wet dispersion mode. The XRD patterns were recorded using Bruker AXS instrument equipped with Cu Kα ($\lambda = 1.5406$ Å) radiation operating at 40 kV and 40 mA between 2θ in the range of 5° and 70° with a scan speed of 0.05° s^{-1}. Nitrogen adsorption–desorption isotherms were measured at −196°C by Beckmen-Coulter surface area analyzer (SA^{TM} 3100 model). Prior to the N_2 adsorption/desorption analysis, the adsorbents were degassed at 200°C for 4 h. 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 4,000 and 450 cm^{-1} region using Perkin-Elmer spectrum one FT-IR spectrometer. The concentration of the dye solution was measured from the absorbance versus known concentration calibration curve obtained using UV–vis spectrometer (Perkin Elmer, Model: Lamda 35) by

measuring the maximum absorbance at the wavelength, λ_{max}, of 582 nm. Calibration curve was established prior to the analysis. Calibration ranges for the CV dye was between 2.45×10^{-6} and 4.90×10^{-5} M. Dilutions were performed where necessary to bring the analyte solutions within the calibration range. pH of the solution was measured using a bench top digital pH meter (Eutech instruments, cyberscan pH 510 model).

Adsorption isotherm experiments

Adsorption isotherm experiments were conducted in batch mode. The CV dye was first dried at 100°C (melting point = 205°C) for 2 h to remove the moisture. A stock solution having concentration of 2.45×10^{-3} M was prepared and the experimental solutions were obtained by successive dilutions of the stock solution to a desired concentration. For adsorption isotherm experiments, dye solutions (50 ml) of known initial concentrations (between 4.90×10^{-5} and 7.35×10^{-4} mol l^{-1}) were shaken with 0.05 g of adsorbent (CAL BC and UNCAL BC) in an incubator shaker (Labtech®, Korea) at 150 rpm for 4 h at the natural pH of the dye solution (pH = 5.86). The adsorbent and the CV dye solution were separated by centrifugation at 8,000 rpm for 30 min at room temperature 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 at the maximum wavelength, λ_{max}, of 582 nm spectrophotometrically. The separated adsorbents from the centrifuge were collected and dried at 100°C for FT-IR analysis. The experiments were carried out at three different temperatures (30, 40, and 50°C) in order to determine the effect of temperature on adsorption and the thermodynamic parameters. The effect of pH on percentage removal of CV dye on CAL BC and UNCAL BC was carried out in the pH ranges between 2 and 11 at three different temperatures (30, 40, and 50°C) for the initial dye concentration of 2.45×10^{-4} M. The pH was adjusted by adding few drops of NaOH or HCl to reach a desirable value, before shaking. After adjusting the pH of the CV dye solution, 0.05 g of adsorbent was added into a 50 ml of dye solution and the pH was not controlled after initiation of the batch experiments. All the adsorption experiments were always carried out in duplicate and the mean values were reported. The percentage difference was calculated and plotted as error (as positive and negative error) for the experimental data (error was less than ±6%). A blank experiment was carried out using 50 ml of CV dye solution (concentration = 7.35×10^{-4} mol l^{-1}) in a 250-ml conical flask without any adsorbent to check the control of the experiment. No detectable dye was adsorbed on the wall of the conical flask.

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 (l), m is the mass of the adsorbent (g), C_0 and C_e are the initial and equilibrium concentrations of the dye, respectively.

Isotherm and thermodynamic parameters assessment methods

Langmuir, Freundlich, and Redlich–Peterson models were fitted for data obtained from the adsorption equilibrium experiments. All the models were fitted in nonlinear form to avoid any linearization errors in the correlation coefficients (R^2) (Vasanthkumar 2006).

The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites and is represented by the following equation (Langmuir 1915):

$$q_e = \frac{Q_{max}K_L C_e}{(1 + K_L C_e)} \tag{2}$$

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 l^{-1}), Q_{max} is the maximum adsorption capacity (mol g^{-1}) and K_L is the constant related to the free energy of adsorption (l mol^{-1}).

The Freundlich isotherm is an empirical equation used for non-ideal adsorption on heterogeneous surfaces and is represented by the following expression (Freundlich 1906):

$$q_e = K_F C_e^{1/n} \tag{3}$$

where K_F is the Freundlich isotherm constant (mol g^{-1} (l mol^{-1})$^{1/n}$), which is an indicative of the extent of adsorption (i.e., adsorption capacity) and $1/n$ is the adsorption intensity (dimensionless).

The three parameters, Redlich–Peterson isotherm combines the features of both Freundlich and Langmuir isotherms. It is represented by the following equation (Redlich and Peterson 1959):

$$q_e = \frac{K_{RP}C_e}{(1 + \alpha C_e^g)} \tag{4}$$

where K_{RP} and α are the Redlich–Peterson constants and g is the exponent which lies between 0 and 1. For $g = 1$, the above equation reduces to Langmuir form. This model can describe the adsorption process over a wide range of concentrations.

The thermodynamic parameters, change in Gibbs free energy (ΔG^0), change in enthalpy (ΔH^0) and change in

entropy (ΔS^0), were determined by the following thermodynamic relations:

$$\Delta G^0 = -RT \ln K_L \tag{5}$$

$$\Delta H^0 = -R\left(\frac{T_2 T_1}{T_2 - T_1}\right) \ln\frac{K_1}{K_2} \tag{6}$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \tag{7}$$

where R is the gas constant (8.314 J 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.

Results and discussions

Adsorbent characterization

Thermogravimetric analysis curve for the UNCAL BC is presented in Fig. 1. The UNCAL BC loses its weight in three different temperature regions during calcination. The first region of weight loss (40–100°C) is attributed to the loss of physisorbed water on the surface without any structural modification. The second weight loss between 400 and 560°C is due to the loss of structural water, i.e. loss of OH groups attached to Al and Si (Brown and Gallagher 2003; Viswabaskaran et al. 2003; Jahan et al. 2008). The third region of weight loss (560–750°C) is attributed to further dehydroxylation of the UNCAL BC (Brown and Gallagher 2003; Viswabaskaran et al. 2003). No significant weight loss is observed at higher temperature (>750°C) for UNCAL BC. It confirms that there is no phase change above 750°C (Viswabaskaran et al. 2003). The changes in the TGA for the UNCAL BC are also observed in the first derivative curve (see Fig. 1) and the three distinct weight losses due to reaction/phase transformation are found at 70, 510 and 650°C. As the temperature increases, the clay particles begin to melt and fill the pore spaces which in turn decrease the pore volume of the calcined mixed clay. Calcination decreases the amount of hydroxyl groups, which may decrease the adsorption capacity of the dyes on the adsorbent (Dogan et al. 2000). The inset of Fig. 1 shows the particle size distribution of UNCAL BC. A typical bimodal distribution is observed having a mean particle size of 4.365 μm. Generally, powders having bimodal distribution will affect the adsorption of dye molecules due to their two different particle regimes (coarser and finer). However, in this case, there is no complete separation of two regimes and hence the adsorption may not be affected.

The XRD patterns of the CAL BC and UNCAL BC are depicted in Fig. 2. The main crystalline phases observed in UNCAL BC are kaolinite and quartz. The disappeared and diffused broadened peaks of UNCAL BC during calcination suggest that the phase transformation leads to an amorphization, which makes the CAL BC more amorphous (Shvarzman et al. 2003). This can be identified by the background noise in the XRD pattern of the CAL BC (see Fig. 2). Calcination reaction of the ball clay produces free silica that is amorphous in nature. However, the crystalline peak of the quartz is not affected during calcinations, which is evidenced by a sharp peak of the CAL BC at a 2θ value of 25°. The decrease in the intensity of the quartz peak suggests that there may be a formation of silanol bridges and the occurrence of free silica.

The nitrogen adsorption–desorption isotherm and pore size distribution of CAL BC and UNCAL BC showed a type-II isotherm (Figure is not presented here) with a hysteresis loop arising from the presence of mesopores. The surface area (14.893 m^2 g^{-1}) and pore volume (3.966 cc g^{-1}) of the CAL BC are found to be lower than
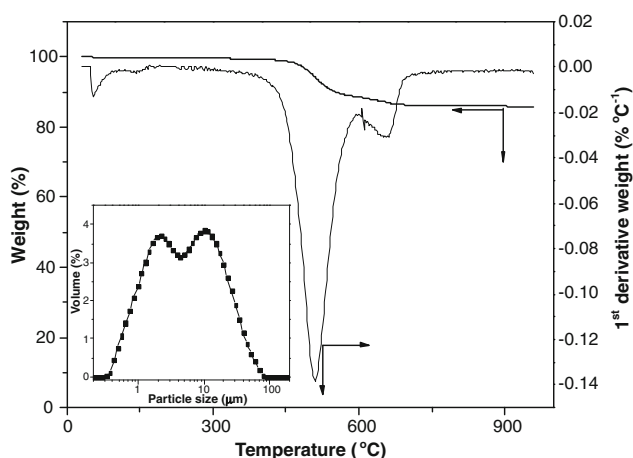

Fig. 1 Thermogravimetric analysis curve of UNCAL BC. *Inset* shows the particle size distribution of UNCAL BC
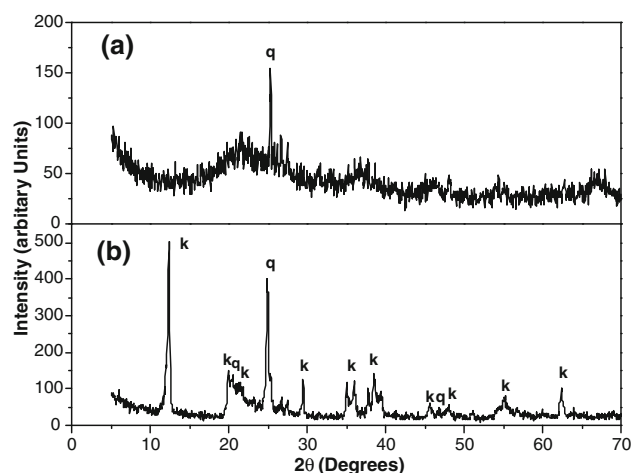

Fig. 2 XRD patterns of **a** CAL BC and **b** UNCAL BC. (*k* kaolinite (PDF 14-164), *q* quartz (PDF 46-1045))

the UNCAL BC (surface area and pore volume of 19.189 m^2 g^{-1}, 4.4087 cc g^{-1}, respectively). The reason for decreased surface area and pore volume of the CAL BC may be due to the formation of the agglomerate structures by partial fusion of particles producing higher amount of coarse fractions (Chandrasekhar and Ramaswamy 2002). In addition, a moderate change in the surface area of the CAL BC indicates that the calcination produces some structural modifications in the UNCAL BC adsorbent (Konan et al. 2009).

Before and after the adsorption of CV dye on CAL BC and UNCAL BC are analyzed using FT-IR spectroscopy and the spectrum is depicted in Fig. 3. FT-IR spectrum measurements are used to study the surface modifications of the adsorbents (Liu et al. 2001). Molecules which are chemically bonded to the clay surfaces will change the FT-IR spectra, whereas molecules adsorbed on the surfaces will have no effect on the FT-IR vibrations of various groups present in the ball clay. The bands at 3695, 3653 and 3620 cm^{-1} of the UNCAL BC are attributed to the elongation vibrations of hydroxyl groups (see Fig. 3b). The band observed at 3696 cm^{-1} is due to the contribution of the hydroxyl groups sitting at the edges of the clay platelets. The bands at 3668 and 3653 cm^{-1} correspond to hydroxyl groups at the surface of the octahedral layers that interact with the oxygen atoms of the adjacent tetrahedral layers. The band appeared at 3620 cm^{-1} is connected with the internal hydroxyl groups. The band observed at 3453 cm^{-1} corresponds to the O–H stretching of the silica group formed by the coupling molecules present in the surface of clays. Changes in the Al–OH vibration band are observed at 2,924 and 2,851 cm^{-1}. The band at 1,115 and 1,034 cm^{-1} correspond to the Si–O and Si–O–Si elongation vibrations, respectively. The band at 913 cm^{-1} is attributed to the deformation vibrations of hydroxyl groups, Al–O–H sitting on the alumina faces (Konan et al. 2009). The bands at 794 and 697 cm^{-1} correspond to Si–O–Al vibrations and the translational hydroxyl group.

The bands at 3668, 3653, and 3620 cm^{-1} correspond to the hydroxyl groups present in the UNCAL BC, which are disappeared in the FT-IR spectrum (see Fig. 3a) of the CAL BC. This indicates that the calcination removes most of the hydroxyl groups that might contribute in the adsorption of dye molecules. The removal of adsorbed water and decrease in the intensity of SiO–H stretching band (3,447 cm^{-1}) indicates the reduction of surface hydroxyl group, which will have detrimental effect on adsorption of dye molecule. Calcination induces a deformation in the silica tetrahedra, which is observed by a shift in the Si–O–Si elongation band from 1,034 to 1,095 cm^{-1}. The fairly intense and narrow band at 794 cm^{-1} of the UNCAL BC is shifted and formed a broad band at
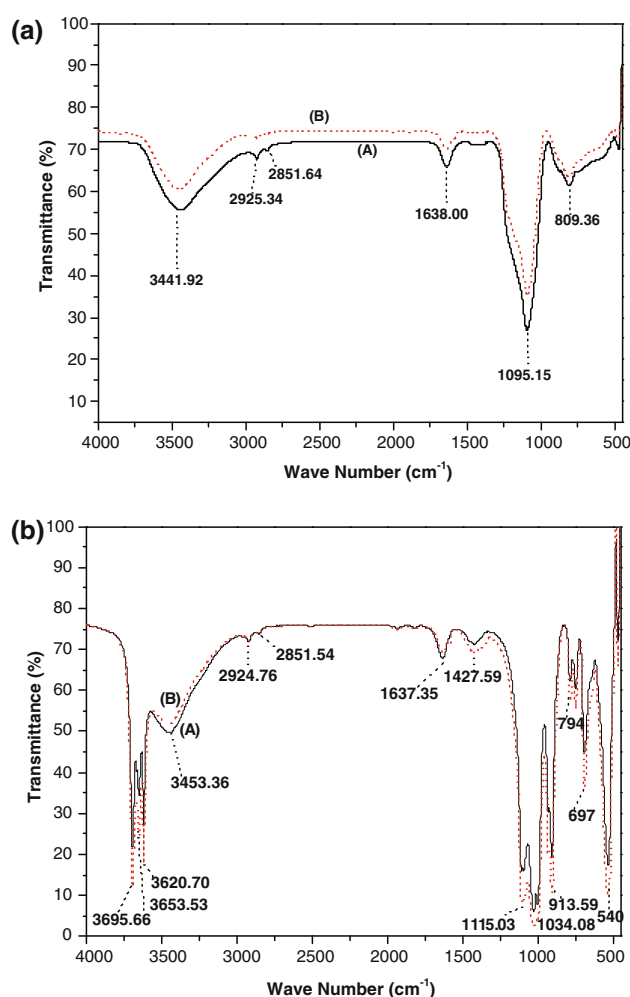
Fig. 3 FT-IR spectra of **a** CAL BC and **b** UNCAL BC. (*A*) Before CV dye adsorption and (*B*) After CV dye adsorption

809 cm^{-1}, which indicates the degree of disorder of the CAL BC. Therefore, calcination leads not only to dehydroxylation but also leads to the structural modification of UNCAL BC.

Adsorption isotherms

The results of equilibrium isotherm experiments are fitted with Langmuir, Freundlich, and Redlich–Peterson models as depicted in Fig. 4. The model parameters obtained by nonlinear curve fitting method are presented in Table 1. The adsorption of CV dye on both the CAL BC and UNCAL BC is found to be increased (see Fig. 4; Table 1) with an increase in the temperature. It indicates that the interaction energy between CV dye and adsorbents is very strong with increase in the temperature. The maximum adsorption capacity of the CAL BC and UNCAL BC is found to be 1.6×10^{-4} and 1.9×10^{-4} mol g^{-1}, respectively at 50°C. The decreased adsorption capacity
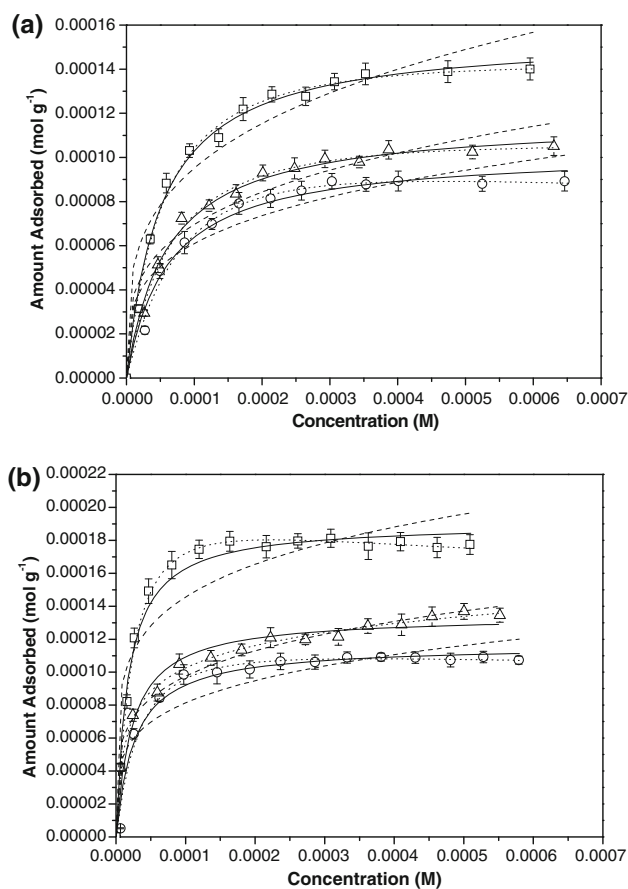
Fig. 4 Adsorption of CV dye at different temperatures on **a** CAL BC and **b** UNCAL BC. (*open circle* 30°C, *open triangle* 40°C, *open square* 50°C, *continuous line* Langmuir model, *dashed line* Freundlich model, *dotted line* Redlich–Peterson model)

tetrahedrally and octahedrally coordinated Lewis base sites that are previously hydrated with hydroxyls of the water molecules (Gucek et al. 2005). The decrease in the adsorption capacity of CAL BC is attributed to the decrease in the tetrahedrally and octahedrally coordinated binding sites due to calcination. After CV dye adsorption, the increase in the intensity of the FT-IR bands (see Fig. 3b) at 3695, 3653, 3620, 1115, 1034, 913, 540 cm^{-1} for the UNCAL BC suggests that the clay is properly dispersed in the dye solution and forms platelets. The adsorption of the CV dye takes place at both the surface and edges of the hydroxyl group present in the UNCAL BC. There is no much variation (shift) in the FT-IR spectra indicating that the CV dye molecules are adsorbed on the surfaces. However, the adsorption takes place on the Si–O–Si and SiO–H bridges only in the CAL BC (see Fig. 3a). Therefore, the adsorption of CV dye on CAL BC is found to be less compared to UNCAL BC. Moreover, the reduction in the number of active sites decreases the adsorption capacity of the CAL BC. The results also reveal that both the electrostatic and hydrophobic interaction (due to the low-density permanent negative charge of silica surface) takes place between the CV dye molecule and UNCAL BC whereas only electrostatic interaction arises in CAL BC. The maximum adsorption capacity of the present work is compared with other adsorbents reported in the literatures as given in Table 2. From Table 2, it is clear that the adsorption capacity of both CAL BC and UNCAL BC adsorbents are comparable with the other adsorbents. The results show that calcination does not bring any improvement in the adsorption capacity of the CV dye on ball clay. Therefore, it is better to use the ball clay as adsorbent without calcination for the removal of CV dye.

Thermodynamic parameter studies

The thermodynamic parameters for the adsorption of CV dyes on CAL BC and UNCAL BC are calculated as presented in Table 3. The negative value of ΔG^0 at all the temperatures suggests that the adsorption of CV dye on both the adsorbents is thermodynamically feasible and spontaneous in nature. There is no significant change in the ΔG^0 values at temperatures studied for CAL BC and UNCAL BC, which results in very less changes in the adsorption capacity. The positive values of ΔH^0 indicate that the adsorption is endothermic in nature. The positive ΔS^0 value of both the adsorbents stipulates an increase in the randomness at the solid–solution interface. The interaction in the CAL BC is strong (due to electrostatic interaction) than the UNCAL BC (both electrostatic interaction and n–π interaction), so that the values of ΔS^0 of CAL BC (104.29 J mol^{-1} K^{-1}) is slightly lower than the UNCAL BC (112.30 J mol^{-1} K^{-1}).

for CAL BC over the UNCAL BC is due to the reduction in the surface hydroxyl group, surface area, and pore size of the adsorbent during calcination. Similar observations were also reported for the adsorption of dye on perlite, kaolin, and diatomite (Dogan et al. 2000; Ghosh and Bhattacharyya 2002; Khraisheh et al. 2005). The correlation coefficients (R^2) of both the Langmuir and Redlich–Peterson models are greater than the Freundlich model at temperatures studied, which implies that the adsorption isotherm follows monolayer adsorption. So Langmuir and Redlich–Peterson model could better describe the adsorption of CV on CAL BC and UNCAL BC. The "g" values of the Redlich–Peterson model are close to 1 indicating that some heterogeneous pores or surface of the ball clay will play a major role in the dye adsorption. Although the surface of the clay is structurally heterogeneous in nature, the adsorption of the dye will take place on the active sites (hydrophilic edges) of the clay, which is homogeneous in nature (Somasundaran and Hubbard 2006). As a result, the dye molecules may adsorb on the edge of the crystal, which forms a binding with the

Table 1 Adsorption isotherms parameters of CV dye on CAL BC and UNCAL BC at different temperatures at pH = 5.86

Adsorbent	Isotherm model	Parameters	Temperature (°C)		
			30	40	50
Calcined ball clay	Langmuir Model	Q_{max} (mol g^{-1})	1.0×10^{-4}	1.2×10^{-4}	1.6×10^{-4}
		K_L (l mol^{-1})	1.639×10^4	1.665×10^4	1.957×10^4
		R^2	0.981	0.992	0.993
	Freundlich Model	K_F (mol g^{-1} (l mol^{-1})$^{1/n}$)	0.73×10^{-3}	0.88×10^{-3}	1.24×10^{-3}
		$1/n$	0.27	0.28	0.28
		R^2	0.909	0.940	0.935
	Redlich–Peterson Model	K_{RP} (mol g^{-1})	1.19	1.65	2.66
		α ((l mol^{-1})^g)	4.84×10^4	2.52×10^4	2.69×10^4
		g	0.99	0.98	0.98
		R^2	0.992	0.994	0.995
Uncalcined ball clay	Langmuir Model	Q_{max} (mol g^{-1})	1.2×10^{-4}	1.3×10^{-4}	1.9×10^{-4}
		K_L (l mol^{-1})	3.798×10^4	4.345×10^4	5.883×10^4
		R^2	0.978	0.977	0.985
	Freundlich Model	K_F (mol g^{-1} (l mol^{-1})$^{1/n}$)	0.63×10^{-3}	0.69×10^{-3}	0.81×10^{-3}
		$1/n$	0.222	0.212	0.185
		R^2	0.864	0.982	0.876
	Redlich–Peterson Model	K_{RP} (mol g^{-1})	3.35	13.40	8.03
		α ((l mol^{-1})^g)	6.08×10^4	3.69×10^4	10.12×10^4
		g	0.99	0.872	0.98
		R^2	0.984	0.996	0.998

Table 2 Adsorption capacity of CV on various adsorbents

| Adsorbent	Adsorption capacity (mol g^{-1})	Operating conditions	Reference
Activated carbon from sewage sludge	1.67×10^{-4}	$T = 30°C$ and pH = 6	Graham et al. 2001
Activated carbon from coconut husk	1.51×10^{-4}	$T = 30°C$ and pH = 6	Graham et al. 2001
Unexpanded perlite	8.10×10^{-6}	$T = 30°C$ and pH = 11	Dogan and Alkan 2003
Expanded perlite	2.80×10^{-6}	$T = 30°C$ and pH = 11	Dogan and Alkan 2003
Bagasse fly ash	6.43×10^{-5}	$T = 30°C$	Mall et al. 2006
Activated carbon (PAAC)	1.48×10^{-4}	$T = 28°C$ and pH = 6	Senthilkumaar et al. 2006a, b
MCM-22	1.20×10^{-4}	$T = 30°C$ and pH = 6	Wang et al. 2006
Jute fiber carbon	0.68×10^{-4}	$T = 32°C$ and pH = 8	Porkodi and Vasanthkumar 2007
Palygorskite	1.42×10^{-4}	$T = 25°C$ and pH = 6	Al-Futaisi et al. 2007
Raw sepiolite	1.80×10^{-4}	$T = 36°C$ and pH = 6	Eren and Afsin 2007
Raw kaolin	1.10×10^{-4}	$T = 26°C$ and pH = 7	Nandi et al 2008
CAL BC	1.00×10^{-4}	$T = 30°C$ and pH = 5.86	Present work
UNCAL BC	1.20×10^{-4}	$T = 30°C$ and pH = 5.86	Present work

Effect of pH

The effect of pH on the percentage removal of the CV dye from aqueous solution using CAL BC and UNCAL BC adsorbents is depicted in Fig. 5. From Fig. 5, one can observe that both the CAL BC and UNCAL BC follow the same trend for the removal of CV dye from aqueous solution. The percentage removal of CV increases with an increase in the pH from 2 to 11 and a maximum removal (94–98%) are obtained at pH 11. When the pH increases, the number of negative sites on the surface of the clays also increases, which consecutively increases the adsorption of

Table 3 Thermodynamic parameters for the adsorption of CV on CAL BC and UNCAL BC

Adsorbent	ΔG^0 (KJ mol^{-1})			ΔH^0 (KJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
	30°C	40°C	50°C		
CAL BC	−24.45	−24.29	−26.54	7.21	104.29
UNCAL BC	−26.56	−27.79	−29.47	17.46	112.30
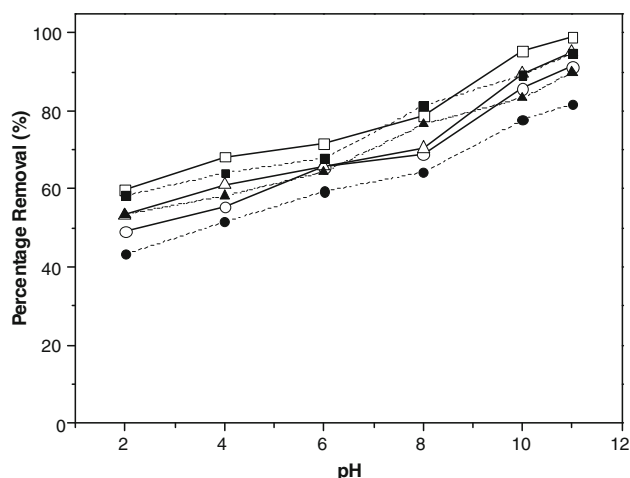
Fig. 5 Influence of pH for CV dye adsorption on CAL BC (*open circle* 30°C, *open triangle* 40°C, *open square* 50°C) and UNCAL BC (*filled circle* 30°C, *filled triangle* 40°C, *filled square* 50°C)

the CV dye on CAL BC and UNCAL BC due to the presence of excess hydroxyl group. The siloxane bond of the CAL BC and UNCAL BC is also cleaved by the sodium hydroxide at higher pH. This phenomenon also increases the adsorption capacity of the CV dye at higher pH on both the adsorbents. Similar observations for the adsorption of CV on kaolin and diatomite were also reported in the literatures (Ghosh and Bhattacharyya 2002; Khraisheh et al. 2005). Based on the result, it is clear that the adsorption process is highly dependent on the pH of the solution.

Conclusion

The applicability of locally available ball clay as an adsorbent in its raw and calcined form for the removal of CV dye has been investigated. The TGA result reveals that the UNCAL BC undergoes various reactions/phase transformations during calcinations. It is observed that the surface area and the pore volume of CAL BC decrease during calcination. The adsorption capacity of both the CAL BC and UNCAL BC increases with increase in the temperature and pH of the dye solution. The adsorption capacity of the UNCAL BC (1.9×10^{-4} mol g^{-1}) is found to be higher

than that of the CAL BC (1.6×10^{-4} mol g^{-1}) at 50°C. The reduction in the adsorption capacity of CAL BC is mainly due to decrease in the surface area, pore volume and surface hydroxyl group. The adsorption isotherm matches very well with the Langmuir and Redlich–Peterson model than the Freundlich model. Thermodynamic parameters indicate that the adsorption is spontaneous and endothermic in nature. The obtained result reveals that the calcination of ball clay does not show any increase in the adsorption capacity of the CV dye. It indicates that the CAL BC is not an efficient and economic adsorbent for the removal of CV dye. Based on the investigation, it can be concluded that UNCAL BC would be used as an alternate for the expensive activated carbon.

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