Synthesis of malachite@clay nanocomposite for rapid scavenging of cationic and anionic dyes from synthetic wastewater

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ABSTRACT

Synthesis of malachite@clay nanocomposite was successfully carried out for the removal of cationic (Methylene Blue, MB) and anionic dyes (Congo Red, CR) from synthetic wastewater. Nanocomposite was characterized by TEM, SEM, FT-IR, EDS analysis and zeta potential. TEM analysis indicated that the particle diameter of nanocomposite was in the range of 14 to 23 nm. Various important parameters viz. contact time, concentration of dyes, nanocomposite dosage, temperature and solution pH were optimized to achieve maximum adsorption capacity. In the case of MB, removal decreased from 99.82% to 93.67% while for CR, removal decreased from 88.55% to 75.69% on increasing dye concentration from 100 to 450 mg/L. pH study confirmed the higher removal of CR in acidic range while MB removal was higher in alkaline range. Kinetic study revealed the applicability of pseudo-second-order model for the adsorption of both dyes. Negative values of ΔG° for both systems suggested the feasibility of dye removal and support for spontaneous adsorption of CR and MB on nanocomposite. Nanocomposite showed 277.77 and 238.09 mg/g Langmuir adsorption capacity for MB and CR respectively. Desorption of dyes from the dye loaded nanocomposite was easily carried out with acetone. The results indicate that the prepared malachite@clay nanocomposite is an efficient adsorbent with high adsorption capacity for the aforementioned dyes.

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INTRODUCTION

Water pollution by variety of pollutants due to increased industrial activities has attracted attention of scientists worldwide. Different industries such as textile, tannery, pharmaceutical, printing, leather and food industries extensively use different kinds of dyes in variety of applications (Chan et al., 2016; Jia et al., 2016; Liu et al., 2015). Among the numerous aqueous pollutants, dyes have aroused increasing public concerns due to their toxic nature and several studies showed that dyes can be carcinogenic and mutagenic and can cause harmful effects even if present in very low concentrations (Asfaram et al., 2015; Chan et al., 2016; Dhananasekaran et al., 2016; Shayesteh et al., 2016; Srilakshmi and Saraf, 2016). Dyes are photochemically stable and their presence in water bodies prevents sunlight penetration and disturbs the photosynthetic activities of aquatic life (Banerjee et al., 2014; Madrakian et al., 2012). Hence, treatment of dye-laden wastewater by an efficient technique is essential. Various techniques such as photodegradation, oxidation, membrane separation, adsorption, coagulation, electrolysis and photocatalysis and

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biological treatment have been utilized during the last few decades (El-Gamal et al., 2015; Jia et al., 2016; F. Zhang et al., 2016; Y. Zhang et al., 2016) but most of them are not much efficient. However, among various treatment techniques, adsorption technique has proven to be an effective technique for the abatement of different kind of dyes and variety of other pollutant species from effluents due to its operational simplicity, high efficiency and low energy requirements (Mane and Vijay Babu, 2013; Zeng et al., 2014). Further, application of low-cost adsorbent makes it a suitable treatment technology especially for the developing nations. Dyes adsorption on activated carbon has been extensively explored through the past few decades but the main drawback related with activated carbon is its high cost which restricts its largescale application and warrant for search of new, low-cost adsorbent materials for this purpose (Weng and Wu, 2011). Several studies are available on the application of low-cost adsorbents for the treatment of dyes (Banerjee et al., 2014; Gupta and Suhas, 2009). Due to low-cost, clay particles have been frequently used for the treatment of variety of dyes and have been proved as an efficient adsorbent for dyes (Bulut et al., 2008; Lian et al., 2009a; Toor et al., 2015; Weng and Pan, 2007). But recently, application of adsorbents incorporated with nanoparticles has received considerable attention due to their enhanced adsorption efficiency (Asfaram et al., 2015; Chang et al., 2016; Liu et al., 2015). This article presents synthesis of malachite@clay nanocomposite for the abatement of Methylene Blue (MB, cationic dye) and Congo Red (CR, anionic dye) from synthetic wastewater. Bentonite clay was selected for malachite loading. The use of nontoxic precursors for nanocomposite synthesis makes it an environmental friendly adsorbent material, which is the need of the safe treatment process. The impact of various important parameters on removal of cationic (MB) and anionic dyes (CR) were studied. Kinetic, thermodynamic and isotherm studies were conducted. Regeneration of dye loaded malachite@clay nanocomposite was also examined. Various research studies have been carried out with bentonite and modified bentonite, but synthesis of nanocomposite by using bentonite clay has rarely been reported. In the present study, malachite nanoparticles have been developed on bentonite surface, which drastically affected the adsorption efficiency of adsorbent for both cationic and anionic dyes as well.

1. Materials and methods

1.1. Details of synthesis method of malachite@clay nanocomposite

The synthesis of malachite@clay nanocomposite was carried out by precipitation method. For this purpose, both copper sulphate and sodium carbonate solutions were prepared in ethylene glycol. Molar ratio of copper sulphate solution and sodium carbonate solution was kept to be 1:2 (Molchan et al., 2008; Srivastava et al., 2015). To get malachite (\(\text{Cu}_2\text{(OH)}_2\text{CO}_3\)) nanoparticles, dropwise addition of copper sulphate solution in to sodium carbonate solution was carried out and this mixture solution was continuously stirred on a magnetic stirrer. The greenish precipitate thus obtained confirmed the formation of malachite particles. This solution was stirred for 30 min and thereafter, 4 g of bentonite clay was added into the above solution and again stirred for 90 min for the interaction of bentonite with the surface group of malachite nanoparticles. Bentonite clay was sieved by 150 μm mesh sized sieve prior to its use to get uniform sized bentonite particles. In the beginning, the colour of bentonite clay was grey but after 90 min stirring, greenish coloured malachite@clay nanocomposite was formed. This nanocomposite was separated from ethylene glycol by centrifugation (Eppendorf 5810R) at 5000 r/min for 10 min and then washed many times with deionized water. Finally, the precipitate was washed by ethanol and dried at 333 ± 0.5 K in hot air oven. A tube mill (IKA Tube mill control) was used for the grinding of dried nanocomposite to crush the lumps of particles and to get fine powder. Synthesized malachite@clay nanocomposite was characterized by several techniques. Transmission electron microscopic (TEM) images of bentonite and malachite@clay nanocomposite were captured by Hitachi H-7700. Scanning electron microscopic images (SEM) and Energy dispersive X-ray analysis was carried out by scanning electron microscopic attached with EDAX unit (S-4800, Hitachi, Japan). The Fourier transform infrared spectra (FT-IR) of bentonite clay, malachite@clay nanocomposite and dye loaded nanocomposite were collected in the frequency range from 4000 to 400 cm\(^{-1}\) (Bruker Vertex 70 model, Sweden).

1.2. Batch adsorption experiments for dye removal

The removal efficiency of synthesized malachite@clay nanocomposite for MB and CR dyes was investigated by conducting batch mode adsorption experiments. A stock solution with 1000 mg/L concentration of Methylene blue (\(\text{C}_16\text{H}_{18}\text{N}_3\text{SCl}\)) and Congo red (\(\text{C}_32\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2\)) was prepared separately by mixing of dye powders in deionized water. Stock solution of MB and CR was further used by proper dilution to get different dye concentrations. For the determination of equilibrium time for adsorption of both dyes, dye solutions were agitated (at 200 r/min) with 2 g/L of adsorbent on a temperature controlled shaker for different time intervals. Dye samples were collected at different time intervals and adsorbent was separated from dye samples by centrifugation for 10 min at 4000 r/min. After centrifugation, clear supernatant was collected in different vials for the analysis of residual dye concentration which was measured by a UV–Vis spectrophotometer at the \(\lambda_{\text{max}}\) of 668 nm for MB and 497 nm for CR. The pH of dye solutions was maintained by adding 0.1 mol/L HCl/NaOH. Different adsorbent dose ranges (1 to 10 g/L) were tested for both dyes to demonstrate the effect of dose on removal of dyes. Temperature of dye solution was maintained in the range of 293 ± 0.5 to 313 ± 0.5 K to observe the effect of temperature on removal of dyes. A comparative study for adsorption capacity of malachite@clay nanocomposite and bare bentonite clay was also carried out. pH study was carried out from pH 5.0 to 10.0 for CR and pH 2.5 to 10.0 for MB. Following equations were used for calculating the removal percentage and amount of dye adsorbed per unit mass of adsorbent at any time (\(q_t\))

\[
\text{Removal of dye} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100\%
\]

\[
q_t = \left(\frac{C_0 - C_t}{m}\right)V
\]
where, \( C_0 \) (mg/L) and \( C_t \) (mg/L) represent the initial dye concentration and dye concentration at time \( t \) respectively. \( V \) (L) and \( m \) (g) denote the volume of dye solution and weight of the adsorbent respectively.

For kinetic study, dye adsorption on nanocomposite was carried out at 300 mg/L dye concentration. Isotherm study for both systems was conducted at 293 ± 0.5 K temperature with dye solution of different concentrations varying from 100 to 450 mg/L (without adjusting the pH of solution) and 2 g/L adsorbent dose. For isotherm study, 180 min contact time was taken for adsorption experiments.

### 1.3. Desorption study

For desorption study, malachite@clay nanocomposite was loaded with dyes in optimized adsorption conditions for maximum adsorption. The dye loaded sample was collected and washed with deionized water for the removal of any adherent particles of dyes on the surface of nanocomposite. After several times of washing, washed nanocomposite was kept in oven at 60°C for drying. Subsequently, it was used for desorption study. Different desorption mediums were selected for dye desorption (0.5 mol/L HCl, NaOH, CH\(_3\)COOH, C\(_2\)H\(_5\)OH, 1:1 mixture of C\(_2\)H\(_5\)OH:HCl (5 mL of each solvent), acetone and ethylene glycol). Dye loaded adsorbent was agitated for 4 hr with 2 g/L adsorbent in different desorbing mediums at 293 ± 0.5 K and 200 r/min. After desorption, regenerated adsorbent was separated from desorbing medium and then dried after proper washing with deionized water. Regenerated adsorbent was reused for further adsorption cycles. Three successive adsorption–desorption cycles were investigated for the determination of reusability of nanocomposite. The percentage of desorption was measured using the following Eq. (3) (Khan et al., 2015):

\[
\text{Desorption} = \left( \frac{\text{Concentration of dye desorbed}}{\text{Concentration of dye adsorbed}} \right) \times 100\%
\]

### 2. Results and discussions

#### 2.1. Adsorbent characterization

TEM images of bentonite clay and malachite@clay nanocomposite were captured by adjusting acceleration voltage at 100 kV and the average particle diameter of nanocomposite was determined by TEM image. In TEM image of bentonite clay, particles with different morphologies can be seen (Fig. 1a and b) while most of the particles in malachite@clay nanocomposite have similar morphology (Fig. 1c and d). Particle diameter of nanocomposite was in the range of 14 to 23 nm. Elemental analysis of bentonite clay and malachite@clay nanocomposite particles was examined by energy dispersive X-ray spectroscopy (EDS) analysis. Detailed composition of bentonite clay and malachite@clay nanocomposite with EDS diagram is shown in Fig. 2a and b. Weight % of Cu and O element is higher in nanocomposite which shows the presence of Cu\(_2\)(OH)\(_2\)CO\(_3\) with bentonite clay. SEM images of bentonite clay, bare malachite@clay nanocomposite and dye loaded nanocomposite were recorded at an acceleration voltage of 100–150 kV for the study of surface morphology. SEM images of bentonite clay and malachite@clay nanocomposite clearly indicate the presence of malachite particles on bentonite clay (Fig. 3a, b).

Bentonite clay has different oxide groups, but when it is dissolved in Cu\(_2\)(OH)\(_2\)CO\(_3\) solution during synthesis process, its oxide groups interact with -CO\(_3\) and OH\(^-\) groups of Cu\(_2\)(OH)\(_2\)CO\(_3\) (Gupta et al., 2015; Şahin et al., 2015; Saikia et al., 2013).

Flat surfaces which are present in bare nanocomposite, disappeared after dye loading, which shows that some part of bentonite clay which was not loaded with malachite nanoparticle was also involved during adsorption process and hence disappeared in loaded samples (Fig. 3c, d). However, most of the particles still showed the same morphology. Particle size calculated from SEM images supports the TEM results. The FT-IR spectra of bentonite clay and malachite@clay nanocomposite and dye loaded nanocomposite were also analysed (Appendix A Fig. S1).

In FT-IR of bentonite clay, the absorption peak at around 3623.82 cm\(^{-1}\) showed the stretching vibrations of -OH groups of bentonite (Toor et al., 2015) and a sharp band around 797.85 cm\(^{-1}\) shows presence of quartz (Gupta et al., 2015). Absorption peaks at 915.22 cm\(^{-1}\), 1000.85 cm\(^{-1}\), 519.22 cm\(^{-1}\) and 1637.26 cm\(^{-1}\) can be assigned to the Al–OH–Al, stretching vibration of Si–O groups, Si–O–Si deformation modes and the OH deformation of water respectively (Gupta et al., 2015; Şahin et al., 2015; Toor et al., 2015). Further, absorption band at 456.24 cm\(^{-1}\) is related to Si–O–Si bending vibrations and the absorption peak at 620.98 cm\(^{-1}\) corresponds to couple Al–O and Si–O out-of-plane vibrations (Şahin et al., 2015). In FT-IR of malachite@clay nanocomposite, absorption peak at 880 cm\(^{-1}\) is due to the characteristic C–C bond and peaks in the range 2800–3000 cm\(^{-1}\) represent the C–H bond (Srivastava et al., 2015). Further, absorption peaks at 3320 cm\(^{-1}\), 1113 cm\(^{-1}\) and 1454 cm\(^{-1}\) are related with the stretching vibration of –OH group, C–O–C and carbonate respectively. Further, absorption peaks at 1597 and 1361 cm\(^{-1}\) are related to anti symmetric (CO\(_3\))\(^2-\) stretching modes. Peaks in the range 2800–3000 cm\(^{-1}\) in malachite@clay nanocomposite were not observed in MB loaded adsorbent.

After adsorption of dyes, peak around 3620.24 cm\(^{-1}\) in MB loaded malachite@clay nanocomposite and peak at 3616.54 cm\(^{-1}\) in CR loaded malachite@clay nanocomposite shows the stretching vibrations of –OH groups of bentonite. During adsorption of CR, carbonate groups of malachite@clay nanocomposite are involved in CR interaction and hence disappear in CR loaded adsorbent. Peaks at 1597 cm\(^{-1}\) are also involved in CR adsorption. New peak was observed at 1332.75 cm\(^{-1}\) in MB loaded nanocomposite, which shows the formation of new bond between adsorbent and MB dye. During adsorption of dye on adsorbent surface, the aromatic ring of dye interacts with the adsorbent surface through the π-electron system of the ring. CR contains charged sulfonated group (–SO\(_3\)Na\(^+\)) in aqueous medium so electrostatic attraction occurs between protonated malachite@clay nanocomposite surface and CR. During adsorption of CR, carbonate groups of malachite@clay nanocomposite are involved in CR interaction which was confirmed by FT-IR spectra of CR loaded adsorbent sample.

#### 2.2. Comparative study for the efficiency of bare bentonite and malachite@clay nanocomposite

For the comparative study of adsorption efficiency of bare bentonite clay and malachite@clay nanocomposite, different
Fig. 1 – (a, b) Transmission electron microscopic image of bentonite clay at different magnifications; (c, d) TEM images of malachite@clay nanocomposite at different magnifications.

Fig. 2 – Energy dispersive X-ray analysis images and composition of (a) bentonite clay and; (b) malachite@clay nanocomposite.
concentrations (25 to 400 mg/L) of MB and CR were selected and agitated with 2 g/L of bentonite clay and malachite@clay nanocomposite for 180 min at 293 ± 0.5 K and then separated from dye solution. UV–Visible spectrophotometer was used for determination of the residual concentration of dyes. The malachite@clay nanocomposite showed enhanced adsorption for both dyes in comparison to bentonite clay (Appendix A Fig. S2). However, malachite@clay nanocomposite was found to be more efficient for MB removal in comparison to CR. When bentonite clay and malachite@clay nanocomposite were compared, the difference between adsorption capacities was higher for CR than MB. Further study was carried out with malachite@clay nanocomposite.

2.3. Study of the effect of adsorbate-adsorbent contact time on the removal of dyes

For removal of any adsorbate molecule, it is necessary to keep appropriate contact time between adsorbate and adsorbent. To determine optimum contact time, nanocomposite was agitated with dye solutions for different time intervals (15–300 min).

Faster removal was observed in the case of MB and >95% removal was observed within 10 min and after 1 hr, there was only slight increment in the removal of MB (Fig. 4). While in the case of CR, only 85% removal was achieved in first 10 min. It was observed that only 60 min of contact time was sufficient for >90% removal of CR. After 180 min, only a slight difference was observed. It can be stated that 180 min was sufficient to get maximum removal of CR (98.25%) and MB (99.94%) hence 180 min contact time was selected for other experiments. At the initial stages, removal was found to be very fast. Rapid removal of dyes at the initial stages of adsorption is due to the presence of ample amounts of free adsorbent sites which are easily accessible and dye molecules easily interact with the available active sites. Whereas the removal of dyes became slower as the time increased, because after a certain time there were not enough available adsorbent sites for remaining dye molecules to get adsorbed.

2.4. Study on the effect of initial concentration on dye removal

To explore the effect of initial dye concentration on adsorption of dyes, initial concentration of dye was varied from 100 to 450 mg/L. Adsorbent dose was kept constant (2 g/L) for each concentration to observe the effect of concentration for particular selected adsorbent dose. It was observed that on
increasing initial dye concentration from 100 to 450 mg/L, percentage removal decreased from 99.82% to 93.67% for MB while for CR, removal decreased from 88.55% to 75.69% (Fig. 5).

However, on increasing dye concentration, the amount of adsorbed dye increased in both cases because at lower concentration, most of the adsorbent sites are left unoccupied while at increased concentration, number of occupied adsorbent sites increased resulting in increased adsorption capacity.

2.5. Study on the effect of nanocomposite dosage on the removal of CR and MB

To explain the effect of malachite@clay nanocomposite dosage on CR and MB, adsorption was conducted at different adsorbent dosages from 1.0 to 10 g/L with the dye solution of 300 mg/L concentration. The adsorption of CR increased from 83.82% to 99.56% while in case of MB, the removal increased from 94.36% to 99.95% (Appendix A Fig. S3). In the case of MB, the adsorption rapidly increased with the increase of dose from 1.0 to 3.0 g/L but after that there was not any significant change in removal. It shows that 2 g/L adsorbent dose is sufficient for selected MB concentration. In the case of CR, 96% of dye molecule was removed from the solution by using 2 g/L of adsorbent dose and then gradually increased up to 10 g/L. Increased removal of dye with increasing adsorbent dose is obvious because higher adsorbent dose facilitate more adsorbent sites for dye molecules. However, adsorption capacity decreased by increasing adsorbent concentration because at high adsorbent dosage, most of the adsorbent sites remain unoccupied and could not reach saturation. As 2 g/L adsorbent dose was found to be quite efficient for significant removal of both dyes, so this dose was selected for all other adsorption experiments.

2.6. Study on the effect of solution pH for dye removal

The pH of solution is an effective parameter, which decides the surface nature of adsorbent and adsorbate in aqueous solution as well as the degree of ionization. The removal study of both dyes were carried out in different pH ranges to observe the behaviour of dye removal in different pH ranges. In the case of MB, pH varied between 2.0 and 10.0 while in the case of CR, pH varied between 5.0 and 10.5. The other experimental conditions were dye concentration 300 mg/L, dose 2 g/L, Temp 293 ± 0.5 K; agitation speed 200 r/min and contact time 180 min. On decreasing the pH of CR solution below 5, its colour changed from red to dark blue, so pH of CR solution was not maintained below 5.0. The resonance among charged canonical structures was responsible for colour changes (Lian et al., 2009a; Purkait et al., 2007).
Fig. 6a and b shows the structure of MB and CR (Ebadi and Rafati, 2015; Mane and Vijay Babu, 2013). CR exists in its anionic form in alkaline medium while it presents its cationic form in acidic medium. CR gives anions when dissolved in aqueous medium while MB gives cations in aqueous medium. Fig. 6c depicts the trend of removal efficiency on variation of solution pH. In acidic medium, adsorbent surface get protonated due to availability of large number of H⁺ ions, and attract available anions from medium. CR is an anionic dye which contains charged sulfonated group (−SO₃Na⁺) in aqueous medium so electrostatic attraction occurs between protonated adsorbent surface and anionic dye, hence higher removal of CR was observed in acidic medium (Bulut et al., 2008). Decreased removal percentage of CR dye was observed when pH of CR solution goes in alkaline range, because in alkaline medium electrostatic repulsion occurred between dye anions and deprotonated adsorbent surface. Further, in alkaline medium the available OH⁻ ions also compete with dye anions resulting in decreased removal of CR in alkaline medium. However, synthesized adsorbent was found to be quite efficient for significant adsorption of CR (>80%) even in the alkaline pH range 7–11. In the case of MB, dye removal increased on increasing solution pH. MB exists in cationic form in aqueous solution. In acidic medium, electrostatic repulsion occurs between protonated surfaces and MB cations, which decrease adsorption of MB in acidic condition. Further, there will be a strong competition between MB cations and H⁺ ions for adsorbent surface in acidic medium. While in alkaline medium, deprotonated surface favours dye cations due to electrostatic attraction between deprotonated surface and MB cations. Similar findings were observed in other studies (Li et al., 2015; Zhou et al., 2015). UV spectra was also collected for the MB and CR solution after adsorption at different pH and it was observed that in the case of CR intensity increased with increase of pH while in the case of MB intensity decreased when pH is increased from acidic to alkaline range (Appendix A Fig. S4). Fig. 6d depicts that zeta potential values of malachite@clay nanocomposite sharply reduced up to 6.0 pH value, then there was a slight decrease from pH 6.0 to 8.0 and then again, a sharp decrease was recorded after 10.0 pH. An isoelectric point of malachite@clay nanocomposite was recorded to be 5.6, which suggests that adsorbent surface gets positively charged when pH of solution is <5.6 which will favour anionic species while at higher pH (>5.6) negatively charged adsorbent surface will favour cationic species hence MB removal was higher in alkaline medium and CR removal was higher in acidic medium.

2.7. Study on the effect of dye solution temperature on MB and CR removal and thermodynamic study

Three different solution temperatures viz. 293 ± 0.5, 303 ± 0.5 and 313 ± 0.5 K were taken under consideration to demonstrate the effect of temperature on dye adsorption (Appendix A Fig. S6a and b). Removal experiments for this study were conducted with varying initial dye concentrations (100 to 450 mg/L). Adsorption capacity slightly decreased with increasing temperature in the case of methylene blue, which suggests that the interactions between the cationic dye and active chemical groups of malachite@clay nanocomposite were lower at higher temperatures (Appendix A Fig. S5a). Decreased MB removal at higher temperature was observed due to Brownian movement and breaking of existing intermolecular hydrogen bonding between MB and malachite@clay nanocomposite. Further, at higher temperature, removal of MB decreased due to high interaction between dyes and solvent in comparison to dye and adsorbent (Aljeboree et al.,...
2014; Li et al., 2013). In the case of CR, enhanced removal was recorded with the increase of temperature from 293 ± 0.5 to 313 ± 0.5 K, which suggests endothermic nature of CR adsorption on nanocomposite (Appendix A Fig. S5b). Adsorbate molecule gets sufficient energy for interaction with adsorbent surface sites. The increase in adsorption capacity of nanocomposite for CR may be due to the pore size enlargement which provides new adsorbent sites for the dye interaction which were not available at lower temperature (Chinoune et al., 2016; Doğan and Alkan, 2003; Yan et al., 2015). Another reason might be de-aggregation of adsorbent at higher temperatures due to which more exposed adsorbent sites were available for dye interaction (Fuo and Hameed, 2010). In this study, effect of temperature is not very significant for lower concentration but as the dye concentration increases, clear difference can be seen in adsorption capacities for both dyes (Appendix A Fig. S4a and b).

Thermodynamic study plays an important role for detailed investigation of any adsorption process. It is possible to explain spontaneity of process, randomness of adsorbate-adsorbent system and endothermic/exothermic nature of adsorption process by determination of thermodynamic parameters viz. changes of Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). Following equations were applied for the calculation of different thermodynamic parameters for present study (Sharma et al., 2007):

\[ \Delta G^0 = -RT \ln k_c \]  \hspace{1cm} (4)

\[ \Delta H^0 = R \left( \frac{T_2T_3}{T_2-T_3} \right) \ln \frac{k_c}{k_c^0} \]  \hspace{1cm} (5)

\[ \Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \]  \hspace{1cm} (6)

where, \( \Delta G^0 \) (kJ/mol), \( \Delta H^0 \) (kJ/mol) and \( \Delta S^0 \) (J/(mol·K)) represent the changes of Gibbs free energy, enthalpy and entropy, respectively. \( R \) is the universal gas constant (8.314 J/(mol·K)); \( K_c \) (= \( C_{ad} / C_d \)) is the distribution coefficient where \( C_{ad} \) (mg/L), and \( C_d \) (mg/L) represent the equilibrium concentration of dye on the adsorbent and in the solution respectively. \( T \) (K) is absolute temperature. Values of \( \Delta G^0 \), \( \Delta H^0 \) and \( \Delta S^0 \) for CR and MB are shown in Appendix A Table S1. Negative value of \( \Delta G^0 \) for both systems indicates the feasibility of dye removal by adsorption on nanocomposite and suggests the spontaneous nature of CR and MB adsorption on nanocomposite. The \( \Delta G^0 \) values for CR revealed that higher solution temperature was more favourable for CR adsorption, while higher removal of MB could be achieved at lower temperatures. Further, the obtained value of \( \Delta G^0 \) is in the range between −20 and 0 kJ/mol, which supports the involvement of physisorption process (Jin et al., 2014). Positive value of \( \Delta H^0 \) in the case of CR suggests the endothermic nature of system while in the case of MB, the value of \( \Delta H^0 \) is negative, which confirms that MB adsorption is an exothermic process. A positive value of the entropy change (\( \Delta S^0 \)) in the case of CR suggests about the randomness at the solid/solution interface which increases during the adsorption of CR dye on nanocomposite (Ghaedi et al., 2015) while the negative value of \( \Delta S^0 \) for MB adsorption on nanocomposite shows that the randomness at the solid/solution interface decreases on increasing the solution temperature.

### 3. Kinetic study

Kinetic study for any adsorption process is useful for understanding the adsorption mechanism of any pollutant species (Wang et al., 2014). Kinetic studies of adsorption were thoroughly performed at 293 ± 0.5 K by taking dye concentration (300 mg/L) for both dyes. Pseudo first-order (Lagergren, 1898; Lian et al., 2009b) and pseudo second-order kinetic (Ho and McKay, 1998) models were used on adsorption data to determine the rate constants. Several steps may be involved in the adsorption of any adsorbate viz. intraparticle diffusion, film diffusion and pore diffusion. To investigate the participation of these mechanisms, intraparticle diffusion model, Boyd model and Bangham’s model were applied on the kinetics of CR and MB on malachite@clay nanocomposite.

\[ \log (q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \]  \hspace{1cm} (7)

where, \( k_1 \) (min⁻¹) represents the pseudo first-order rate constant. \( q_e \) (mg/g) and \( q_t \) (mg/g) are the equilibrium adsorption capacities at equilibrium and at time ‘t’ respectively. Appendix A Table S2 shows the values of \( q_e \) and \( k_1 \) which were determined from the intercept and slope of plots of \( \log (q_e - q_t) \) vs. \( t \) (Fig. 7a). The values of \( R^2 \) were >0.95 for both dyes. However, the value of model calculated \( q_e \) did not agree well with experimental \( q_e \).

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} - \frac{1}{q_e}t \]  \hspace{1cm} (8)

where, \( k_2 \) (mg/(g·min)), \( q_t \) (mg/g) and \( q_e \) (mg/g) represent the pseudo second-order rate constant, the adsorption capacities at any time ‘t’ and at equilibrium respectively. ‘h’ is the initial sorption rate (mg/g min).

The pseudo second-order kinetic parameters were determined from the slope and intercept of plots “t/q_e versus t” (Fig. 7b). The values of \( R^2 \) were found to be >0.99 for both dyes which were higher in comparison to the \( R^2 \) values for pseudo first-order model. Furthermore, in the case of pseudo second order model, the experimental and calculated values of \( q_e \) were very close to each other which also confirmed that the pseudo-second-order model is best for explaining the kinetics of adsorption of both dyes (Appendix A Table S2).

To investigate the participation of intraparticle diffusion mechanism during dye adsorption on malachite@clay nanocomposite, following Weber–Morris equation for intraparticle diffusion was applied on the kinetic data (Reynel-Avila et al., 2016; Wang et al., 2014):

\[ q_t = k_{id} t^{0.5} + C \]  \hspace{1cm} (10)

where, \( k_{id} \) (mg/(g·min¹/²)) represents the intraparticle diffusion constant, \( t \) (min) is the contact time, \( q_e \) (mg/g) denotes the adsorption capacity at time \( t \). \( C \) is related with the boundary layer effects. The values of different intraparticle diffusion parameters (Appendix A Table S2) were determined from the slope and intercept of the plots of ‘\( q_t \) vs. \( t^{0.5} \)” (Fig. 8a). In the case of rate limiting process, intraparticle diffusion plot passes through origin but in this study it was observed that for both dyes, the
linear plot did not pass through the origin, which shows that intraparticle diffusion is not the only rate governing step.

In some cases, film diffusion process may be a rate governing step so to investigate the participation of film diffusion process during dye adsorption, Boyd model was applied on the kinetic data which can be expressed as follows (Boyd et al., 1947):

\[
F = \left(1 - \frac{6}{\pi^2}ight) \exp(-Bt)
\]  

(11)

\[
F = \frac{q_t}{q_e}
\]

(12)

where, \(q_t\) (mg/g) and \(q_e\) (mg/g) denote the quantities of dye adsorbed at any time ‘t’ and at equilibrium respectively. \(B_t\) is denoted as a mathematical function of \(F\).

\[
B_t = -0.4977\ln(1-F)
\]

(13)

\[
B = \frac{a^2D_i}{r^2}
\]

(14)

Boyd plot ‘\(B_t\) vs. \(t\)’ was found to be linear for both dyes which suggests the involvement of film diffusion during dye adsorption (Fig. 8b). For the present adsorbate-adsorbent system, film diffusion process controlled the rate of adsorption of both dyes as the linear plots did not pass through the origin. Value of \(R^2\) was found to be >0.95 which also suggested the applicability of Boyd model on MB and CR adsorption.

During adsorption process, removal of adsorbate species can also proceed via pore diffusion mechanism. The possibility of pore diffusion in dye adsorption process was investigated by applying the following Bangham’s equation (Mane et al., 2007):

\[
\log \left(\frac{\log \left(\frac{C_0}{C_0-q_m}\right)}{\log \left(\frac{C_0}{C_0-q_m}\right)}\right) = \log \left(\frac{k_{0m}}{2.303\ V}\right) + \alpha \log (t)
\]

(15)

where \(k_0\) and \(\alpha(<1)\) are the Bangham constants. \(C_0\) (mg/L), \(m\) (g/L), \(q_m\) (mg/g) and \(V\) (mL) represent the initial dye concentration, weight of adsorbent, the amount of dye adsorbed at time ‘t’ and volume of dye solution respectively. Bangham’s constants were determined from the slopes and intercepts of plot \(\log \left(\frac{C_0}{C_0-q_m}\right)\) versus \(\log(t)\) (Fig. 8c) and the values of Bangham constants \(\alpha\) and \(k_0\) with corresponding \(R^2\) values are presented in Appendix A Table S2. The linear plots for both dyes with good correlation coefficient (>0.9) indicate involvement of pore diffusion.

4. Isotherm study

The adsorption isotherm is helpful in the designing of any adsorption system (Namasivayam and Sureshkumar, 2009). The equilibrium data was analysed by various “two parameter isotherm models” viz. Langmuir, Freundlich, Elovich and Temkin isotherm model.

According to the Langmuir model, monolayer coverage is formed due to adsorbate species on adsorbent surface and transmigration is not possible between adsorbed dye species (Aluigi et al., 2014). Eq. (16) shows the expression for Langmuir isotherm model (Kinniburgh, 1986; Langmuir, 1918):

\[
q_e = \frac{q_mK_aC_e}{1+K_aC_e}
\]

(16)

where, \(q_m\) (mg/g) represents the maximum adsorption capacity of adsorbent and \(K_a\) (L/g) is the Langmuir constant related to the energy of adsorption. \(q_e\) (mg/g) and \(C_e\) (mg/L) are adsorption capacity and concentration of dyes at equilibrium respectively.

The Langmuir isotherm equation can be linearized into four different forms as follows.

\[
\text{Langmuir I } C_e = \frac{1}{q_m}C_e + \frac{1}{K_aq_m}
\]

(17)

\[
\text{Langmuir II } \frac{1}{q_e} = \left(\frac{1}{K_aq_m}\right)\frac{1}{C_e} + \frac{1}{q_m}
\]

(18)

\[
\text{Langmuir III } q_e = q_m\left(\frac{1}{K_a}\right)\frac{q_e}{C_e}
\]

(19)

\[
\text{Langmuir IV } \frac{q_e}{C_e} = K_aq_m - Kaq_e
\]

(20)
To calculate the maximum Langmuir adsorption capacity, equilibrium data was analysed by all the four linearized forms of Langmuir isotherm.

The different isotherm parameters for linearized equations of Langmuir isotherm were determined from the slope and intercept of plot C/qe vs. C e/1/qe, 1/Ce vs. qe/Ce, and qe/Ce vs. qe for Eqs. (17)–(20) respectively (Fig. 9a-d). Values of Langmuir parameters with corresponding R² values are summarized in Appendix A Table S3. qm value calculated from different linearized Langmuir equations is almost in the same range, but highest value of qm was found in the case of Langmuir type I for both dyes. Best fit isotherm model for experimental data can be determined by correlation coefficient (R²) values. It was observed that Langmuir types I and II had good R² values (>0.95) in comparison to Langmuir type III and IV.

The Freundlich isotherm model supports for heterogeneous surface having different adsorption sites and non-uniform distribution of adsorption energy at surface and can be expressed as follows (Freundlich, 1906; Zheng et al., 2009):

\[ q_e = K_f C_e^{1/n} \]  

(21)

The Freundlich isotherm follows the expression on linearization:

\[ \log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e) \]  

(22)

where, \( K_f \) (mg\(^3\)/(L\(^n\)g\(^{-1}\))) represents the Freundlich adsorption capacity while \( n \) is the term used for the heterogeneity factor related to adsorption intensity. Freundlich constant was calculated by the plot 'log(qe) vs. log(Ce)' (Fig. 10a) and its values are shown in Appendix A Table S3.

Elovich isotherm assumes that adsorbent sites increase exponentially with adsorption and multilayer adsorption of adsorbate species is possible. Elovich isotherm can be represented as follows (Hamdaoui and Naffrechoux, 2007)

\[ \frac{q_e}{q_m} = K_E C_e \exp \left( \frac{q_e}{q_m} \right) \]  

(23)

\[ \ln \left( \frac{q_e}{q_m} \right) = \ln (K_f q_m) - \frac{q_e}{q_m} \]  

(24)

where, \( K_E \) (L/mg) and \( q_m \) (mg/g) represent the Elovich equilibrium constant and the maximum adsorption capacity respectively. Elovich isotherm constant was determined from the slopes and the intercepts of the plot ln (qe/Ce) versus qe (Fig. 10b) and presented in Appendix A Table S3.

The Temkin model is described by the following Eqs. (25)–(27) (Mane et al., 2007)

\[ q_e = \frac{RT}{b_T} \ln (K_T C_e) \]  

(25)

\[ q_e = B_T \ln K_T + B_T \ln C_e \]  

(26)

\[ B_T = \frac{RT}{b_T} \]  

(27)

where, \( K_T \) (L/g) is the Temkin isotherm binding constant, \( b_T \) (J/(mol·K)) represents the heat of adsorption, \( R \) (8.314 J)/(mol·K), \( B_T \) is Temkin constant and \( T \) (K) are the universal gas constant and the absolute temperature respectively. Temkin constants calculated from Fig. 10c are given in Appendix A Table S3 with their correlation coefficients.

Among different linearized Langmuir isotherms, Type I and II were found to be suitable for describing isotherm data. Langmuir adsorption capacity calculated from Langmuir Type I equation was highest among all the other linearized forms. Linear plot for type I suggests its suitability for both systems. However, among all the studied isotherms, Freundlich model is most suitable for both dyes with coefficient R² values for MB (>0.98) and CR (>0.99). The following trend was observed for different isotherm models:

Freundlich > Langmuir I > Temkin > Elovich (for MB);
Freundlich > Langmuir II > Temkin > Elovich (for CR).

A comparative study for adsorption capacity of synthesized nanocomposite with other available adsorbents was...
also conducted. Adsorption capacity of malachite@clay nanocomposite for MB and CR is rather comparable with adsorption capacities of other available adsorbent materials (Appendix A Table S4) (Abkenar et al., 2015; Ahmed and Gasser, 2012; Asfaram et al., 2015; Bulut et al., 2008; Chang et al., 2016; Chen et al., 2014; Cottet et al., 2014; Dhananasekaran et al., 2016; Dutta et al., 2015; Ebadi and Rafati, 2015; Hao et al., 2014; Li et al., 2016; Lian et al., 2009a, 2009b; Mahapatra et al., 2013; Ozmen and Yilmaz, 2007; Pal et al., 2015; Shan et al., 2015; Tian et al., 2016; Toor et al., 2015; Vimonses et al., 2009; Wang et al., 2012; Weng and Pan, 2007; Yan et al., 2015). Synthesized malachite@clay nanocomposite was found to be very efficient for the removal of both cationic as well as anionic dyes which supports for its applicability in the treatment of dye laden wastewater.

5. Desorption study of MB and CR

Desorption study showed that among all tested eluents (0.5 mol/L HCl, NaOH, CH₃COOH, C₂H₅OH, 1:1 mixture of C₂H₅OH: HCl, acetone and ethylene glycol), acetone was highly efficient to desorb the maximum amount of dye from dye loaded adsorbent. Similar findings were also reported by other researcher (Chowdhury et al., 2009; Dave et al., 2012). So, acetone was selected as desorbing medium for desorption of dye and regeneration of adsorbent for further adsorption–desorption cycles. Regenerated adsorbent was quite efficient for the removal of both dyes (>55%) up to two adsorption–desorption cycles (Appendix A Fig. S6). However, in third cycle adsorption % decreased to 44% for CR and 48% for MB. Thus further cycles were not investigated.

6. Conclusions

In this paper, malachite@clay nanocomposite was synthesized and characterized by various techniques in order to determine its characteristics. TEM analysis revealed the formation of nanosized particles having diameter in the range of 14–23 nm. Dye removal abilities of malachite@clay nanocomposite were investigated by taking methylene blue and congo red as cationic and anionic model dyes. The as-prepared malachite@clay nanocomposite exhibited
excellent adsorption capacities for wide concentration range from 100 to 450 mg/L for both dyes. Enhanced removal was observed in acidic range for CR, while MB removal was higher in alkaline range. Pseudo-second order kinetic model was found to be suitable for describing the kinetics of CR and MB dyes. The malachite@clay nanocomposite showed adsorption capacity 277.77 mg/g for MB while in the case of CR adsorption capacity was determined to be 238.09 mg/g. Present study suggests that malachite@clay nanocomposite adsorbent could be explored as an exceptionally promising candidate for MB and CR adsorption and can be utilized for the treatment of cationic and anionic dyes from industrial wastewaters.

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Appendix A. Supplementary data
Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.08.011.

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