Adsorptive removal of cationic and anionic dyes using graphene oxide
V. Sabna, Santosh G. Thampi and S. Chandrakaran

ABSTRACT
This paper presents the results of comparative study on the application of graphene oxide (GO) for the adsorptive removal of crystal violet (CV) and methyl orange (MO) in batch mode. GO, synthesised from graphite, was characterised by field emission scanning electron microscopy (FESEM), Fourier transform infrared (FTIR) spectroscopy, point of zero charge (pHpZC) and ultra violet (UV) spectroscopy. Dispersion of GO in water revealed the conversion of hydrophobic graphite into hydrophilic. Performance with regard to adsorption of CV and MO on GO was evaluated at different values of the operational parameters such as contact time between GO and the dye molecules, dosage of GO, and initial concentration and pH of the dye solution. Uptake and percentage removal of the dyes increased with increase in contact time and adsorbent dosage, but declined with increase in initial concentration of the dye. Experimental data on the uptake of dye molecules by GO showed good fit with the Freundlich isotherm model and the pseudo second order kinetic model. The maximum uptake by GO was higher for CV (207.4 mg/g) than that for MO (37.2 mg/g). Results indicate that GO is an effective adsorbent for the removal of CV but not for MO.

Key words | adsorption, crystal violet, methyl orange, graphene oxide

INTRODUCTION
Occurrence of synthetic dyes in water bodies can severely affect not only aquatic animals and plants but also human beings when they come into contact with the human body. The main sources of synthetic dyes in the environment are textile, paper and paint industries, discharging effluents containing these dyes, typically into a water body located nearby. Dyes can be classified as cationic and anionic according to the charge on the dye molecules as it ionises in water; cationic dyes form cations and anionic dyes form anions as they ionise in water. Crystal violet (CV), also known as gentian violet, is a cationic dye used extensively in textile, paper and printing ink industries and also as a biological stain, bacteriostatic agent in veterinary medicine, skin disinfectant in humans etc. It causes cancer, skin and digestive tract irritation and it can persist in the environment since it is poorly metabolised by microbes due to its aromatic structure, which makes it strong and resistant to biodegradation (Mittal et al. 2010). Methyl orange (MO) causes irritation to eyes and skin when coming into contact with it, and causes digestive tract irritation if swallowed. In view of the above, it is very essential to treat the effluents/wastewaters containing these dyes before it is discharged into the environment and to treat water that is contaminated with these dyes. Coagulation (Verma et al. 2012), chemical precipitation (Wang et al. 2015), membrane filtration (Rashidi et al. 2015; Thamaraiselvan & Noel 2015), adsorption (Sabna et al. 2016), solvent extraction (Hu et al. 2005), reverse osmosis (Abid et al. 2012), photocatalytic degradation (Thomas et al. 2014) etc. are the different methods employed in the treatment of effluents/wastewaters containing synthetic dyes. Adsorption has been found to be the most versatile method, and it yields the best results (Rafatullah et al. 2010). Numerous adsorbents and bioadsorbents such as treated ginger waste (Kumar & Ahmad 2011), teak (Patil et al. 2011), bottom ash (Nidheesh et al. 2012), polyaniline/hollow manganese ferrite nanocomposites (Rahimi et al. 2010), functionalised multi-walled carbon nanotubes (Sabna et al. 2016) etc. have been used for the removal of dyes from aqueous solution. Like multiwalled carbon nanotubes, another carbonaceous adsorbent that can be used for the removal of dyes are graphene and its derivatives such as graphene oxide (GO). GO is considered as one of the most significant nanomaterials for the
past few years in the field of nanotechnology and has attracted the scientific community due to its unique two-dimensional structure (Ishigami et al. 2007), large specific surface area (McAllister et al. 2007), good mechanical properties (Papageorgiou et al. 2017), etc. GO is synthesised by the oxidation of GR sheets of sp²-bonded carbon atoms arranged in a honeycomb structure (Ishigami et al. 2007). The large specific surface area, high surface-to-volume ratio, high electrocatalytic activity, superior mechanical properties and outstanding conductivity ensure its potential application in sensors (Kang et al. 2009; Liu et al. 2011), energy storage and conversion (Hass et al. 2008), super capacitors (Shi et al. 2009; Liu et al. 2010; Huang et al. 2012) and nanocomposite applications (Zhiguo et al. 2011, 2012; Feng et al. 2012). GO has been applied for the removal of pollutants in the form of nanocomposites with carbon nanotubes (CNT) and manganese oxide (MnO₂) (Liu et al. 2015), with TiO₂ (Thomas et al. 2014; Wang et al. 2015) through capacitive deionisation (Wimalasiri & Zou 2013). Also, it has been used as a separating layer in GO-polymer membranes and this improved its antifouling properties (Zinadini et al. 2014), hydrophilicity and the salt rejection (Ganesh et al. 2013) of membranes.

In this study, adsorptive removal of CV and MO by graphene oxide has been evaluated as a function of operating parameters such as initial concentration and pH of the aqueous solutions of dyes, dosage of GO, and the contact time between GO and molecules of CV and MO. Equilibrium sorption and kinetic characteristics of the adsorption of CV and MO on to GO in batch mode are also studied.

**MATERIALS AND METHODS**

Potassium permanganate (KMnO₄), sodium nitrate (KNO₃), hydrogen peroxide (H₂O₂) and sulphuric acid (H₂SO₄) procured from Merck were used for the synthesis of GO. GO was synthesised from locally available graphite powder. Potassium nitrate (KNO₃), hydrochloric acid (HCl) and sodium hydroxide (NaOH) used for the determination of pHₚZC were also purchased from Merck. The dyes used as the adsorbate – methyl orange and crystal violet were purchased from SRL. Distilled water was used for washing the synthesised GO and for preparing dye solutions of different concentrations.

**Synthesis of graphene oxide**

Graphene oxide was synthesised from graphite powder using modified Hummer’s method (Shahriary & Athawale 2014). In brief, 1 g of graphite and 0.5 g of sodium nitrate were mixed together followed by the addition of 23 mL of concentrated sulphuric acid under constant stirring. After 1 h, 3 g of KMnO₄ was added gradually to the above solution while keeping the temperature at less than 20 °C to prevent overheating and explosion. The mixture was stirred at 35 °C for 12 h and the resulting solution was diluted by adding 500 mL of water under vigorous stirring. To ensure the completion of reaction with KMnO₄, the suspension was further treated with 30% H₂O₂ solution (5 mL). The resulting mixture was washed with HCl and then with H₂O, followed by filtration and drying. The synthesised GO was stored for characterisation and for the batch mode experiments on the adsorptive removal of CV and MO.

**Characterisation of GO**

A scanning electron microscope (FESEM-HITACHI SU 6600) with variable pressure field emission was used for the analysis of surface features of graphite and GO. The samples of graphite and GO were sputter coated with gold for 40 s with a sputtering unit to induce electrical conductivity. An electron voltage of 5 kV was applied and images were taken at 50 times magnification. The point of zero charge (pHₚZC) is the pH at which the material has a net zero surface charge, and is an important factor for any material that acts as an adsorbent; the process occurring is a function of surface area. pHₚZC was determined following the literature (Oliveira et al. 2010) A portion of 0.005 g GO was put into each of a set of five 50 mL Erlenmeyer flasks, each containing 10 mL of an electrolyte (0.03 M KNO₃ solution). The pH of the solutions was adjusted to a range from 2.5 to 11.5 using dilute aqueous HCl or NaOH. All the flasks were then shaken in an orbital shaker for 24 h at 250 rpm. After shaking for a period of 24 h, all the flasks were kept undisturbed for 1 h, after which the final pH of all the solutions was measured using a pH meter (Eutech). A graph was plotted between pH_initial and pH_final of the KNO₃ solutions and of the GO-KNO₃ solution mixture. pHₚZC of the materials is obtained from the graph where the two curves intersect each other. Fourier transform infrared (FTIR) spectra of GO were recorded on a JASCO FTIR-4100 spectrophotometer using potassium bromide (KBr) as the mulling agent to characterise the chemical bonds in GO. Ultraviolet-visible (UV-Vis) spectra of the samples were obtained (UV-Vis spectrophotometer Perkin-Elmer LAMBDA 35).
Batch adsorption experiments

Batch adsorption experiments were conducted with a working volume of 10 mL of dye solutions (CV and MO) with concentrations of 20 to 150 mg/L; adsorbent dosage of 0.5 to 2 g/L and at pH 4 to 9.5. The samples were analyzed for the residual concentration of CV and MO at specific time intervals until equilibrium was reached, using a UV-Vis spectrophotometer (Perkin Elmer – LAMDA 35) at characteristic wavelengths - 590 nm for CV and 450 nm for MO. The percentage removal of the dye (%R) and the amount of dye adsorbed per unit weight of the adsorbent (mg/g) at equilibrium, \( q_e \), are obtained using the equations

\[
\%R = \frac{C_i - C_t}{C_i} \times 100
\]

\[
q_e (mg/g) = \frac{C_i - C_t}{m} v
\]

where \( C_i \) (mg/L), \( C_t \) (mg/L) and \( C_e \) (mg/L) are the concentrations of the dye initially, at time \( t \) and at equilibrium respectively, \( m \) (g) is the mass of the adsorbent and \( v \) (L) is the volume of the dye solutions.

Kinetic analysis of the adsorption of CV and MO onto GO was performed with the pseudo first order (PFOM) and pseudo second order (PSOM) kinetic models, which are presented below.

Pseudo first order (PFOM) \( \ln (q_e - q_t) = \ln q_e - k_1 t \)

Pseudo second order (PSOM) \( \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \)

The terms \( C_0 \) and \( C_i \) in the equations are the concentrations of CV at time \( t = 0 \) and \( t = t \) respectively. \( q_t \) (mg/g) and \( q_e \) (mg/g) are the amount of the dye at time \( t \) and at equilibrium respectively, \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g/mg min) are the rate constants in the respective kinetic model equations. Linear equations of each of the models were plotted and the parameters of the models were determined.

Adsorption isotherm analysis was carried out by fitting the experimental data on the uptake of dyes onto GO to the Langmuir and Freundlich isotherm models. The Langmuir model assumes monolayer adsorption on a structurally homogeneous adsorbent, where all the sorption sites are identical and energetically equivalent. Adsorption occurs at specific homogeneous sites and once a dye molecule occupies a site, no further adsorption can take place at that site (Langmuir 1916). The Freundlich model assumes a heterogeneous adsorption surface and an exponential distribution of active sites (Freundlich 1907). The linear forms of the Langmuir and Freundlich isotherm models are presented below.

Langmuir isotherm model: \( \frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \)

Freundlich isotherm model: \( \log q_e = \log K_F + \frac{1}{n} \log C_e \)

The terms in the Langmuir adsorption isotherm model, \( q_e \) (mg/g) and \( C_e \) (mg/L) are the uptake and concentration of dye at equilibrium, \( q_m \) (mg/g) is the maximum adsorption capacity and \( K_L \) (L/mg) is the Langmuir constant related to the free energy of adsorption. The separation factor, \( R_L \), is a dimensionless constant that characterises the Langmuir isotherm and indicates whether the adsorption process is favourable \((0 < R_L < 1)\), linear \((R_L = 1)\), unfavourable \((R_L > 1)\) or irreversible \((R_L = 0)\).

\[
R_L = \frac{1}{1 + K_L C_0}
\]

where \( C_0 \) (mg/L) is the highest initial concentration of the dye.

The terms in the Freundlich adsorption isotherm model, \( C_0 \) (mg/g) and \( C_e \) (mg/L), are the uptake and concentration of dye at equilibrium; \( K_F \) (mg/L/g)\(^{1/n}\) is the Freundlich isotherm constant, indicative of the adsorption capacity; \( 1/n \) is the adsorption intensity, which should have a value in between 0.1 and 1 for favourable adsorption.

RESULTS AND DISCUSSION

Scanning electron microscopic analysis

The results of morphological analyses of GO and graphite are presented in FESEM micrographs in Figure 1(a) and 1(b) respectively. The FESEM image revealed the structure of graphite as clumped graphene layers. The graphene layers could not be seen separately in Figure 1(b) whereas, from the FESEM image of graphene oxide given in Figure 1(a), different layers of graphene oxide could be observed. This may be due to the repulsion induced by the negative charges between the oxidised layers of GO.

Dispersion of GO

In water, hydrophilic GO forms a very stable suspension compared to hydrophobic graphite which repels water (Figure 1(c)). This reveals the formation of GO. The functional groups attached onto the graphene layers are very much hydrophilic and these attract water molecules
Figure 1 | FESEM images of (a) GO, (b) graphite, (c) suspension of GO and graphite in water, (d) FTIR spectra of GO and graphite, and (e) pH\textsubscript{ZPC} and (f) UV-Vis spectra of GO.
around, thereby changing the hydrophobic graphite to hydrophilic (Hegab & Zou 2015). This was proved by Prince et al. by improving the hydrophilic nature of membranes by incorporating GO (Prince et al. 2016).

**FTIR analysis**

The important peaks observed in the FTIR spectra of GO and graphite are presented in Figure 1(d) and Table 1. The spectra of graphite did not show any characteristic peak, whereas well-defined peaks of GO could be identified in the FTIR spectra of GO. The FTIR spectrum of GO shows a broad peak between 3,000–3,700 cm$^{-1}$ at 3,442 cm$^{-1}$ corresponding to the stretching vibration of -OH groups of functional groups, or maybe due to water molecules occluded/adsorbed in GO layers (Ganesh et al. 2013). This was absent in the case of graphite, which repels water. Therefore, it can be concluded that the sample has strong hydrophilicity. This also demonstrates the oxidation of graphite to form GO. The presence of an absorption peak at 1,033 cm$^{-1}$ corresponds to the stretching vibration of C=O of carboxylic acid and C-OH of alcohol, respectively (Thomas et al. 2014). The sharp peak at 1,690 cm$^{-1}$ can be attributed to the stretching vibration of C=O of carboxylic acid and carbonyl groups present at the edges of GO (Thomas et al. 2014); the peak at 1,548 cm$^{-1}$ shows the skeletal vibration of the C=C bond in graphene (Guo et al. 2009). The polar groups, especially the surface hydroxyl groups, result in the formation of hydrogen bonds between graphite and water molecules; this further explains the hydrophilic nature of GO.

**Determination of pH$_{PZC}$**

The pH$_{PZC}$ of GO was determined from the graph plotted between the pH$_{initial}$ and pH$_{final}$ of KNO$_3$ and a mixture of KNO$_3$ and GO (Figure 1(e)). pH$_{PZC}$ is given by the point where the two curves intersect each other. Here, the pH$_{PZC}$ of GO is observed at pH 3.9. Thus, it is expected that the surface will have a net positive charge below pH 3.9, and a net negative charge above pH 3.9. Therefore, it can be expected that GO will attract the positively charged CV molecules more to their surface than the negatively charged MO (Saha & Pal 2014).

**UV-Visible spectrophotometric analysis**

UV absorbance spectra of GO were found to show a maximum absorbance peak at ~226 nm attributable to $\pi$-$\pi^*$ transition of the atomic C-C bonds and a shoulder peak at ~302 nm due to n- $\pi^*$ transitions of aromatic C-C bonds (Xu et al. 2013). Similar results were reported earlier (Shahriary & Athawale 2014). The absorbance spectra of graphite did not reveal any characteristic peak at this wavelength, which indicates the formation of GO from graphite. This is evident from Figure 1(f).

**Effect of contact time**

The effect of contact time between GO and dye molecules on the adsorptive removal of CV and MO from aqueous solution of different concentrations was carried out at ambient temperature of 30 °C and the results are presented in Figure 2(a) and 2(b). The adsorbent dosage used in the experiments was 0.5 g/L. During the adsorption process, samples of aqueous solutions of dyes were taken at 5 min, 10 min, 20 min, 40 min and 60 min for the determination of percentage removal of dyes at these time intervals. Equilibrium of adsorption was reached within 10 min and 30 min for the adsorption of MO and CV onto GO. The faster adsorption process in the initial stages is due to the presence of a large number of vacant sites on the surface of GO; later the percentage removal decreases and the adsorption process becomes less efficient due to more and more of these sites being occupied; equilibrium is reached within approximately 20 min for MO and within 40–60 min for CV. After this equilibrium period, the amount of dye adsorbed does not show time-dependent change. The two stage sorption mechanism, with the first rapid and quantitatively insignificant has been reported elsewhere (Saeed et al. 2005). The faster attainment of equilibrium in the case of adsorption of MO onto GO indicates that within the contact time, the adsorbate could not occupy the remaining vacant sites due to high repulsive forces between the molecules of the dye at the adsorbent surfaces and in the bulk solution. Similar results were obtained for the removal of CV by coniferous pinus bark powder (Ahmad 2009).

**Table 1**  Frequency and type of bonds obtained from FTIR spectra

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Type of bonds</th>
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<tbody>
<tr>
<td>3,442 (3,200–3,600)</td>
<td>O-H stretch, H-bonded (strong, broad)</td>
</tr>
<tr>
<td>1,690 (1,670–1,820)</td>
<td>C=O stretch (strong)</td>
</tr>
<tr>
<td>1,033 (1,000–1,300)</td>
<td>C-O stretch</td>
</tr>
<tr>
<td>1,548</td>
<td>Skeletal vibration of GO</td>
</tr>
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</table>
Complete removal was observed for the adsorption of 20 mg/L CV with a dosage of 0.5 g/L of GO; it reached equilibrium within 30 min due to the presence of an excess number of adsorption sites. The adsorption capacity of GO for MO was less than that for CV. Only about 43% removal was observed for MO at a concentration of 20 mg/L. This may be due to the anionic nature of MO and GO, which may repel each other and effective adsorption may not take place.

**Effect of dosage**

Surface area and the availability of binding sites on the adsorbent are the two factors that influence the adsorption process and these increases as the dosage of the adsorbent increases. So dosage is an important factor influencing the adsorption process. The effect of adsorbent dosage of GO on the adsorptive removal of CV and MO was investigated by performing experiments at different adsorbent dosages.
0.2–0.9 g/L for aqueous solution of CV with a concentration of 50 mg/L and 0.4–2.0 g/L for aqueous solution of MO with a concentration of 50 mg/L at an ambient temperature of 30 °C. The results obtained are presented in Figure 2(c) and 2(d). Percentage removal of the dye increased with increase in dosage of GO from 62 to 98% in the case of CV, and 35 to 60% in the case of MO as the dosage increased. This is due to enhancement in the adsorbent specific surface area and the availability of adsorption sites on the adsorbent as the dosage of the adsorbents is increased. Uptake of CV and MO by GO decreased with increase in the amount of adsorbent at constant concentration and volume of aqueous solutions of dyes. This may be attributed to saturation of adsorption sites due to particulate interaction such as aggregation (Aksakal & Ucun 2010). Such saturation of adsorption sites consequent to aggregation leads to a reduction in the total surface area of the adsorbent and increase in the diffusional path length (Crini et al. 2007).

Effect of initial concentration

The effect of the initial concentration of CV and MO on percentage removal of CV and MO by GO was investigated, with values of the initial concentration of aqueous solutions of CV and MO ranging from 20 mg/L to 150 mg/L at an ambient temperature of 30 °C. The results of the study are presented in Figure 2(e). Percentage removal decreased with increase in the initial concentration of the dye for both CV and MO. When the concentration of CV was increased from 20 mg/L to 150 mg/L, percentage removal of the dye decreased from 100% to 31% for an adsorbent dosage of 0.5 g/L. In the case of MO, percentage removal decreased from 43% to 15% when the initial concentration was increased from 20 mg/L to 150 mg/L. This is because when the concentration of an aqueous solution of dyes is lower, the adsorption sites are in excess compared to the concentration of the dye molecules so adsorption takes place very rapidly. Similar results were obtained for the removal of CV by adsorption on to coniferous bark powder (Ahmad 2009).

Effect of stirring

The effect of stirring the mixture of GO and aqueous solutions of CV and MO with a concentration of 10 mg/L at ambient temperature of 30 °C with a dosage of 0.5 g/L of GO were investigated. Increase in the rate of stirring enhances the dispersion of GO uniformly in the reaction mixture, so that all dye molecules become available for the GO to be in contact with them. The effect of dispersion of the particles in the reaction mixture was examined by varying the rate of stirring from 200 rpm to 1,000 rpm. It was observed that increasing the rate of stirring can affect adsorption of CV and MO (Figure 2(f)). Percentage removal increased as the rate of stirring increased.

Effect of presence of ions

Many organic and inorganic molecules may be present in wastewater effluents containing synthetic dyes. The presence of monovalent ions like Na⁺ and Cl⁻ and divalent ions like SO₄²⁻ can hinder the removal of dyes by adsorption onto GO, by competing for the adsorption sites on GO. The effect of the presence of monovalent ions like Na⁺ and Cl⁻ and divalent ions like SO₄²⁻ on the adsorptive removal of CV and MO by GO was investigated at two concentrations of NaCl and Na₂SO₄, 250 mg/L and 500 mg/L. Results of the study are presented in Figure 3(a) and 3(b). From the figures it can be observed that the presence of NaCl reduced the removal of MO (50% to 35%) and CV (95.9% to 93.8%) respectively by adsorption onto GO, whereas the increase in concentration of Na₂SO₄ increased the percentage removal of MO and CV.

Kinetic analysis

Pseudo first order (PFOM) and pseudo second order (PSOM) kinetic models were applied for the kinetic analysis of the adsorption of CV and MO by GO. The coefficient of determination for the pseudo second order model was close to one for adsorption with GO for both MO and CV. Parameters of the pseudo first and pseudo second order kinetic models such as \( q_t \) (mg/g), \( q_e \) (mg/g), \( k_1 \) (min⁻¹) and \( k_2 \) (g/mg-min) and coefficients of determination of CV and MO were obtained by plotting the linear equations of these models (Table 2) respectively. The amount of dye degraded per unit weight of GO, \( q_t \) (mg/g) was estimated for each of the models. It is observed from Figure 4 that the estimated values for \( q_t \) (mg/g) obtained for the pseudo second order kinetic model best suited the experimental data on \( q_t \) (mg/g).

Adsorption isotherm analysis

An adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid phase at a constant temperature and pH (Ho et al. 2003; Allen et al. 2004). The applicability of an adsorbent in an ideal adsorption system can be explored by assessing the most appropriate
equilibrium adsorption correlation (Srivastava et al. 2006). This is essential for reliable prediction of adsorption parameters and quantitative comparison of the behaviour of an adsorbent in different adsorbent systems under different experimental conditions. It describes how pollutants interact with the adsorbent material and facilitates elucidation

Table 2 | Parameters of kinetic analysis of adsorption of CV and MO by GO

<table>
<thead>
<tr>
<th>Initial concentration (mg/L)</th>
<th>$q_e$ Exp (mg/g)</th>
<th>$q_e$ cal. (mg/g)</th>
<th>$k_1$ (min$^{-1}$)</th>
<th>$R^2$</th>
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<tr>
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<td>45.7</td>
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<td>75</td>
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<td>150</td>
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Coefficient of determination of linear kinetic models - CV

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<th>Initial concentration (mg/L)</th>
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<td>38.31</td>
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Coefficient of determination of linear kinetic models - MO

Figure 3 | Effect of presence of ions on the adsorptive removal of (a) MO and (b) CV.

Table 2 | Parameters of kinetic analysis of adsorption of CV and MO by GO

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Coefficient of determination of linear kinetic models - CV

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<td>0.909</td>
<td>35.21</td>
<td>0.025</td>
<td>0.998</td>
</tr>
<tr>
<td>150</td>
<td>37.2</td>
<td>41.36</td>
<td>0.122</td>
<td>0.76</td>
<td>38.31</td>
<td>0.010</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Coefficient of determination of linear kinetic models - MO

Figure 4 | Comparison of $q_t$ obtained from pseudo first order and pseudo second order kinetic models with that obtained by the experimental analysis with GO for (a) MO and (b) CV. (Dosage – 0.5 g/L, and initial concentration – 100 mg/L).
of the adsorption mechanism pathways, estimation of the surface properties and capacities of adsorbents and effective design of systems employed for the removal of specific constituents by adsorption. The estimated values of the parameters and coefficients of determination from the equilibrium plots of Langmuir and Freundlich isotherms are listed in Table 3. Linear plots of Langmuir and Freundlich isotherm models of the adsorption of CV and MO on GO are presented in Figure 5.

As the values of $R_L$ lie in between 0 and 1 for the Langmuir model and the values of $1/n$ lie between 0.1 and 1.0

### Table 3

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Parameter and value</th>
<th>Regression coefficients and constants of isotherm models of adsorption of CV and MO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_m$ (mg/g), $K_L$ (L/mg), $R^2$</td>
<td>CV: 250, 0.153, 0.956; MO: 41, 0.07, 0.998</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$ (mg/g (L/mg)$^{1/n}$), $R^2$, $1/n$</td>
<td>CV: 73, 0.999, 0.239; MO: 9.8, 0.944, 0.283</td>
</tr>
</tbody>
</table>

**Figure 5** | Linear plots of (a) Langmuir, (b) Freundlich adsorption isotherm models of MO, (c) Langmuir, (d) Freundlich adsorption isotherm models of MO.

**Figure 6** | Comparison of $q_e$ obtained from Langmuir and Freundlich adsorption isotherm models for (a) MO and (b) CV.
for the Freundlich model for both CV and MO, it can be concluded that the adsorption process is favourable for both CV and MO. Although the equilibrium data fitted well to both the Langmuir and Freundlich adsorption isotherm models, the Freundlich model exhibited a better fit to the adsorption data than the Langmuir model based on modelled values of uptake by the non-linear form of the models by GO. This indicates the heterogeneous nature of adsorption sites of GO. $q_t$ obtained from the Langmuir and Freundlich isotherm models of adsorption of MO and CV on GO are compared with those from the experimental data (Figure 6(a) and 6(b) respectively).

**CONCLUSIONS**

Graphene oxide (GO) was used in this study to evaluate its adsorption characteristics with reference to removal of CV and MO from aqueous solutions. FESEM images revealed characteristic changes in the structure of GO from the graphite from which it had been synthesised. Characteristic peaks could be observed from the FTIR spectra of GO that were absent in the spectra of graphite. pH$_{PZC}$ of GO was found to be at pH 3.9, below which the surface of GO is expected to be positively charged and above which it is negatively charged. The absorbance spectra of GO in aqueous solution revealed a characteristic peak of GO at 220 nm. Conversion of graphite into GO was also confirmed by its hydrophilicity. Uptake and percentage removal of the dye increased with increase in contact time, and adsorbent dosage but declined with increase in initial concentration of the dye. Presence of inorganic ions like Na$^+$ and Cl$^-$ adversely affect the removal of CV and MO from their aqueous solution medium. Experimental data on the uptake of CV and MO by GO fitted the Langmuir and Freundlich isotherm models and the pseudo second order kinetic model very well; the maximum uptake of CV by GO was 207.4 mg/g and that of MO by GO was 37.2 mg/g. Results indicate that GO is an effective adsorbent for the removal of CV, but it is not effective in the removal of MO from aqueous solutions.

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**REFERENCES**


Kumar, R. & Ahmad, R. 2011 Biosorption of hazardous crystal violet dye from aqueous solution onto treated ginger waste (TGW). Desal. 265, 112–118.


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