Methylene blue (a cationic dye) adsorption performance of graphene oxide fabricated Fe-Al bimetal oxide composite from water

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ABSTRACT

Graphene oxide (GO) fabricated iron-aluminium oxide (GO@IAO) nanocomposite was synthesized with one-spot chemical reaction from emulsification of GO (1.0 g) in 0.2 L of 1.0 M mixed metal solution, which was characterized with some of the latest analytical tools aiming to assess methylene blue (MB) adsorption performance from aqueous solutions. Adsorption of MB on GO@IAO surfaces shows a steep increase from pH 3.0 to 5.0, but steepness declines at pH > 5.0. The closeness of fitted kinetic data with the pseudo-second order (PSO) equation ($R^2 = 0.9845$) compared to the pseudo-first order equation ($R^2 = 0.9527$) confirms the adsorption process is of the PSO type. The MB adsorption equilibrium data can be described better by the Langmuir isotherm ($R^2 = 0.99$) than the Freundlich isotherm ($R^2 = 0.96–0.97$), inclining to the monolayer adsorption process. The Langmuir adsorption capacity of GO@IAO has been estimated to be 330.35 mg/g at 303 K. The MB adsorption is established to be spontaneous ($\Delta G^0 = -26.31$–$-26.61$ kJ/mol) owing to favourable enthalpy and entropy changes ($\Delta H^0 = -23.38$ kJ/mol; $\Delta S^0 = 0.01$ kJ/mol/K). Both absolute and aqueous (1/1, v/v) alcohols regenerate the MB adsorbed GO@IAO up to 80–85%, indicating recyclability of composite.

Key words | adsorption, composite, GO@iron-aluminium oxide, kinetics, thermodynamics

INTRODUCTION

Dyes, a class of synthetic organic compounds, are used in large quantities by different industrial sectors such as textiles, paper, plastic, ink, rubber, concrete etc. for colour. Discharges of the excess dye with waste effluent from those industrial sectors ultimately contaminate the surface water, which is not only unsafe for restoration of the green environment but is also toxic and harmful to aquatic as well as human lives (Li et al. 2016). According to the Colour Index, about ten thousand types of dye have been manufacturing with worldwide production amounts in excess of $7 \times 10^5$ tons per annum (Ahmad et al. 2015). Depending upon the nature the dyes are, in general, divided into anionic, cationic and non-ionic, which are associated with chromophoric and auxochromic groups. Some of the intensely coloured dyes when dispersed into water show visual colour even in trace levels, which blocks the penetration of sunlight from reaching the bulk of the affected water system. In consequence, the levels of dissolved oxygen (DO) decrease while those of biochemical oxygen demand (BOD) increase in contaminated water bodies (Ahmad et al. 2015). The toxicity level of a particular dye and its substrates is very important due to the diverse effect on environment and living organisms. Study of the harmful effects of dye constituents and their metabolites is very important for the establishment of strategies to reduce their toxic effects.

In order to control the negative impacts of dyes on living organisms, several techniques and methodologies (Ahmad et al. 2015) have been developed for the removal of dyes from industrial effluents and other water bodies. The
widely employed technologies for dye removal are surface adsorption (Santos & Boaventura 2008; Li et al. 2011; Du et al. 2014), photocatalytic degradation (Kar et al. 2009; Gulshan et al. 2011), biological treatment (El-Naas et al. 2009), membrane filtration (Kumar et al. 2015) and coagulation-flocculation (Sadnournohamadi & Gorczyca 2015). Although the methods noted above have their own inherent merits and demerits (Hameed 2009; Salleh et al. 2011), adsorption has been proved to be an effective alternative owing to its cheapness, good efficiency, simple operation and low space requirement for installation (Biswas et al. 2010). Sometimes only one technology may not be sufficient for the treatment of dye-rich wastewater, and thus the combination of more than one method is required depending upon the nature of dyes, impurities and composition of the wastewater (Biswas et al. 2010).

Methylene blue (MB), a common cationic dye, finds wide application in biology, medicine, redox titration, dyeing of cotton and silk, colouring paper and so on. The MB contaminated effluent when discharged to water imparts a strong pH dependent colour. Long periods of exposure may lead to effects of hypertension, vomiting, nausea and anaemia (Hameed 2009; Foo & Hameed 2012). Thus, researchers have attempted to develop advanced materials to scavenge MB efficiently for adsorption technology. The adsorbate molecules or ions (liquid or gas) should be concentrated over the material surface (stationary phase) making the adsorbate species free from the liquid or gas phase (mobile phase). It has been thought to be the simplest approach for scavenging dissolved organics from water. Here, the binding of adsorbate species may occur with physisorption or chemisorptions depending on the nature of adsorbate species and solid surfaces. The forces which operate to fix up the solute on surfaces of the adsorbent may be the intermolecular hydrogen bond, electrostatic interaction (ion-ion or ion-dipole), van der Waal forces, hydrophobic interaction etc. Initial dye concentration, solution pH, temperature, contact time, adsorbent nature and adsorbent dosage are usually the prime factors that govern the performance of any adsorption process. Keeping in mind all these variables, different groups of authors used activated carbon (Hameed et al. 2007a, 2007b; Joseph et al. 2007; Hameed 2009; Pathania et al. 2017), polyaniline (Ayad & Ahmed 2010), Fe@C magnetic nanocapsules (Li et al. 2016), graphene oxide (GO) (Ramesha et al. 2011; Yang et al. 2011; Liu et al. 2012), magnetic polysaccharide-GO composite (Gao et al. 2015) and cellulose-GO fibre (Chen et al. 2016) as the solid matrix for concentrating MB from contaminated water. Recently, several groups of researchers have investigated GO and reduced graphene oxide (rGO) for dye removal from aqueous solutions, exploiting their active functionalities and large specific surface area (Ramesha et al. 2011; Yang et al. 2011; Liu et al. 2012; Sharma & Das 2013; Hosseinabadi-Farahani et al. 2015; Gao et al. 2015; Chen et al. 2016). However, the results of dye removal indicated that the efficiency of GO is much better than rGO. However, GO is difficult to use on a large scale due to its high water dispersibility, which creates problems with separating GO from the dispersed phases (Li et al. 2011) because the surface of GO is rich with a good number of hydrophilic functionalities (C=O, COOH, C-OH, epoxy etc.). Consequently, many authors have made attempts to prepare the composite of GO with other materials, aiming to apply this to water treatment (Gao et al. 2015; Chen et al. 2016). It was also converted to composite with mixed iron-aluminium oxide and investigated for fluoride removal from water (Kanrar et al. 2016). The literature shows no report on the use of GO-iron-aluminium oxide composite for dye removal. Thus, the aim is that the efficiency of GO@iron-aluminium oxide (GO@IAO) nanocomposite (NC) will be investigated for concentrating MB (cationic dye) from the aqueous solution by batch adsorption experiments.

We report herein the results of MB adsorption performances from aqueous solution by GO@IAO NC systematically. The parameters investigated are the effects of composite dosage, pH of solution, time of contact, and concentration of MB and regeneration of the MB adsorbed material. In addition, modelling of the kinetic and the equilibrium data has been reported with thermodynamics including the mechanism of MB adsorption with the GO@IAO NC material.

**MATERIALS AND METHODS**

**Chemicals**

MB (basic blue, chemical formula: C_{16}H_{18}ClN_{3}S·3H_{2}O, M.W.: 373.90) was procured from Merck India (Mumbai).
for the experiments. The structure of MB is shown in Figure 1(a). The delocalized positive charge on the organic framework may play a significant role in keeping the species on the surface of the adsorbent material.

The solution of MB has the value of maximum absorbance in visible range at wave length (λ) 665 nm. A stock solution of MB (100 mg/L) was prepared by dissolving an accurately weighed amount of MB in de-ionized water. This MB solution was diluted to the required concentration level by exact dilution for conducting adsorption experiments.

Graphite flake (GF) used for the GO preparation was purchased from Sigma-Aldrich (India). Other chemicals such as ferric chloride hexahydrate and aluminium chloride hexahydrate, which were used for the material preparation, were purchased from Merck (India). The pH value as required for each solution was adjusted with 0.1 M solution of hydrochloric acid/sodium hydroxide.

Graphene oxide (GO) preparation

GO was prepared by the modified Hummers method (Hummers & Offeman 1958; Titelman et al. 2005; Debnath et al. 2014; Kameda et al. 2015) which has been briefed herein. An exact known mass of GF has been mixed with a 50% weight amount of NaNO3 and concentrated H2SO4 (25 times by volume of GF weight amount). The mixture was stirred magnetically inside a beaker placed in an ice-bath. An exact known amount (three times of GF mass) of KMnO4(solid) was added into this mixture, and mixed vigorously at a temperature below 20 °C. This reaction mixture was continually stirred overnight at room temperature, and again KMnO4(solid) (three times of GF mass) was added into the above mixture, which was stirred for another 2 hours at room temperature, aiming to oxidize the unoxidized or underoxidized GF. De-ionized water was added slowly onto the yellowish paste, maintaining a temperature of about 98 °C. This suspension was stirred further for another 4 hours, and a definite volume (equal to total KMnO4 amount) of 30% H2O2 was added for converting unused KMnO4 to Mn2+ ion. The filtered solid mass was washed with 5% HCl and 30% H2O2 to purify the product from MnO and sulfates. Finally it was dried at 55–60 °C under vacuum and a sheet-like solid mass was obtained and stored inside a desiccator.

GO@iron-aluminium oxide nanocomposite (GO@IAO NC) preparation

The GO@IAO NC was prepared by the method as described by Kanrar et al. (2016). One gram of the GO was dispersed homogeneously by sonication in 200 mL of the metal ions solution (100 mL FeCl3, 100 mL AlCl3, each of 1.0 M in 0.1 M HCl). Aqueous 5.0 M NH3 solution was dropped onto the well stirred mixture until the pH of the supernatant reached ∼7.0. After 24 hours of precipitation, the brown mass was filtered out and washed with de-ionized water to make the mass chloride free. It was dried at 60–65 °C in an air-oven. Finally, the composite was crushed and sieved out for the agglomerated particle of size in the range of 140–290 μm (Figure 1(b)).

Instruments

The pH of every test solution was analysed by a pH meter (DIGITAL μ pH METER, GOLD-533) throughout this work. A powder X-ray diffraction (XRD) pattern of the sample was taken with a Philips PW130 generator. Transmission electron microscopic (TEM) images were recorded on an H800 transmission electron micrograph operated at 200 kV. The samples for TEM analysis were dispersed in isopropanol by sonication, and the drops were cast onto 200 mesh copper grids coated with a

Figure 1 | (a) The structural formula of MB; (b) the scheme of GO@IAO preparation.
porous carbon film. Thermo gravimetric (TG) and differential thermal (DT) analyses of GO@IAO NC sample were carried out using Shimadzu DTG-60H simultaneous DTA-TG apparatus over a temperature range of 30–1,000 °C at a heating rate of 10 °C/minute. UV-VIS spectrophotometer (Intech, INDIA) was used for the colorimetric analysis of MB. The sieves BS 52 and BS 100 were used to screen out the composite particles of size in the range of 140–290 μm for employment of the MB adsorption tests. The pHzpc of GO@IAO NC was analysed by the pH metric method (Kameda et al. 2015).

Adsorption studies

Batch adsorption experiments were carried out by agitating 0.2 g GO@IAO NC per L (except dosage variation) of MB solution at optimized pH (except the pH effect) for 1 hour (except contact time). Here the reaction mixture was placed in a glass container, and agitated at 300 (±10) rpm using a speed adjustable magnetic stirrer at some prefixed temperatures. For the dosage optimization, the mass of GO@IAO was varied from 0.2 to 2.0 g/L of the MB solution at room temperature. For the pH optimization on adsorption of MB by GO@IAO, the adsorption reaction was conducted at ten different pHₐ (i.e., initial) values of MB solution from 3.0 to 12.0 with one unit increase of pH. For the contact time optimization for MB adsorption at pH 9.0 by GO@IAO, the experiments were conducted at two different temperatures (303 and 313 K). The samples were collected at some prefixed time gap from the start (t = zero minute) and analyzed until the plateau appeared (equilibrium attained). Isotherm experiments were also conducted at pH 9.0 by magnetic stirring up to the equilibrium time (45 minutes) taking initial MB concentration (C₀) in the range of 1.0–50.0 mg/L. The isotherm experiments were also conducted for the equilibrium of the reaction at three separate temperatures (30, 45 and 60 °C). Once the agitation period was over, the liquid phase was separated immediately from the suspended solid by filtration using membrane filter and absorbance of the clear filtrate was analyzed using a UV–VIS spectrophotometer at 665 nm. The absorbance value was compared with the standard Beer’s law curve for the analysis of MB concentration.

Calculation

The MB adsorbed amount per gram of GO@IAO NC under our experimental conditions was calculated using the mass balance relations (Equations (1) and (2)):

\[
q_e = \frac{(C_0 - C_e)V}{m} \\
q_t = \frac{(C_0 - C_i)V}{m}
\]

where \(q_e\) is the adsorption capacity (mg/g) at equilibrium, \(q_t\) is the adsorption capacity at time, \(t\). \(C_0, C_e,\) and \(C_i\) (mg/L) are the MB concentrations in solution at the initial stage, equilibrium and any time \(t\), respectively. \(V\) (in L) is the volume of MB solution and \(m\) is the mass (gram) of the GO@IAO NC added for carrying out the experiments.

RESULTS AND DISCUSSION

Characterization of GO@IAO

Preliminary investigation of MB adsorption by the composite and the native mixed iron-aluminium oxide (IAO) samples showed that the adsorbed amount of MB by GO@IAO NC was about 20–30% more than that by pristine mixed oxide. Thus, we have characterized the GO@IAO sample and investigated it for the MB adsorption performance systematically.

Figure 2(a) shows the TEM image of GO@ IAO. The spreading of black colour showed good dispersion of GO over the iron-aluminium oxide surface. The image reflects the presence of tiny particles of size 8–10 nm (off white spots). Figure 2(b) shows the scanning electron microscope (SEM) image of GO@ IAO. From Figure 2(b), it is seen that layer of sheets had placed one over the other. However, no definite morphology of the surface appeared in the SEM image.

Figure 3 shows both TG and DT spectra of IAO (Figure 3(a)) and GO@IAO (Figure 3(b)), respectively. It is seen from the TG spectrum of IAO (spectrum-A) that the loss of weight took place in two stages up to 300 °C. The first stage weight loss below 100 °C is due to the elimination of physically attached water molecules and the second stage weight loss at below 300 °C was due to the elimination of lattice water molecules. The DTA spectrum shown in
Figure 3(a) shows two sharp endothermic signals at around 80 and 250 °C, confirming the weight loss of IAO in two stages. Again, it is seen from the TG spectrum in Figure 3(b) for the GO@IAO NC that the weight loss was relatively slow and steady up to the temperature of 600 °C, due to the loss of strongly hydrogen bonded as well as chemically bound water molecules. The DT spectrum in Figure 3(b) of GO@IAO NC shows a sharp endothermic signal at below 100 °C, presumably due to the elimination of hydrogen bonded water molecules from the surface. However, no endothermic signal was recorded at temperatures around 250 °C (spectrum-B) but the DT of IAO (spectrum A) showed an endothermic signal which clearly indicates the greater thermal stability of GO@IAO NC compared to IAO. This enhanced stabilization is due to the binding of the lattice layer with functional groups of GO sheet.

The powder X-ray diffraction (XRD) pattern provides valuable information about the lattice structure and crystalline/amorphous nature of the material. Figure S1 (available with the online version of this paper) shows the XRD pattern of GO@IAO, which has a characteristic peak pattern of the IAO (Kanrar et al. 2016) but the characteristic peak of GO around the value of 2θ = ~10° is invisible, presumably due to the intercalation of GO sheet inside the IAO lattice.

Figure S2 (available online) shows the Raman spectrum of the GO@IAO NC. The well recognized D (1,354 cm⁻¹) and G (1,600 cm⁻¹) bands of GO are present in this material. However, the value of D and G bands moves to a slightly higher Raman shift than that of the GO, indicating the interaction of GO with mixed oxide particles.

The surface area of any adsorbent material is significantly important in adsorption science. Figure S3 (available online)
shows the plots of N2 (vapour) adsorption–desorption against the relative pressure (P/P₀) of N2(vapour) for (A) GO@IAO and (B) IAO. Analyses of adsorption–desorption data have revealed that the specific surface area of GO@IAO NC is 189.5 m²g⁻¹ (Figure S3(A)), which is significantly higher (∼45%) than the pristine IAO (131 m²g⁻¹) (Figure S3(B)). The surface area of the composite material has been enhanced, supporting incorporation of the GO which is the favourable qualification for a material to be a good adsorbent for surface adsorption.

From the plot of initial solution pH (pHᵢ) versus difference between the pHᵢ and the equilibrium solution pH (ΔpH) values (Figure S4, available online), the pHₑzpC of the as-prepared GO@IAO NC can be assigned to 6.58 as ΔpH = 0. That is, the surface of GO@IAO material should be positive at pH < 6.58 and negative at pH > 6.58. The surface should carry equal amounts of positive and negative charges at pH = 6.58. That is, a cationic dye will be adsorbed by the material at pH > 6.58, while an anionic dye will be adsorbed at pH < 6.58.

**Effect of GO@IAO dose on MB adsorption**

Figure 4(a) shows the changes of MB adsorption amount (qₑ, mg.g⁻¹) with increasing dosage amount (g) of GO@IAO. It is seen that the qₑ has decreased exponentially with the increase of GO@IAO dosage from 0.01 to 0.1 g per 50 mL (i.e. 0.2–2.0 g/L) of MB solution. It implies that the value of qₑ decreases with increasing dosage of adsorbent, which may be due to the decrease of MB⁺ species available per unit adsorption site of GO@IAO.

Increase of the MB removal with the decrease of GO@IAO dosage differs from the reports which were made previously by Gao et al. (2015) and Pathania et al. (2017).

**Effect of pH**

The adsorption reaction between adsorbate and adsorbent is strongly influenced by the solution pH because the adsorbate may have different pH dependent species and the pHₑzpC value of adsorbent material is also important. Here, the MB adsorption by GO@IAO was monitored at an initial solution pH (pHᵢ), ranging 3–11, taking an MB concentration of 2.0 mg/L and a dosage of GO@IAO 0.2 g/L. The results obtained are presented as a function of adsorption amount (qₑ, mg/g) against pHᵢ in Figure 4(b). It is seen that the qₑ values have been influenced significantly by the pHᵢ value of MB solution owing to Coulombic forces between MB⁺ and negative charge density on GO@IAO NC (pHₑzpC = 6.58) with increasing pH of the dye solution. However, the increase of the qₑ values was not steady. The low qₑ value at pHᵢ 3.0 is the consequence of the Coulombic inhibition of MB⁺ by the positive charge of the material surface (Pathania et al. 2017). A sharp increase of qₑ was recorded when the pHᵢ of solution moved up above 4.0 because of the increase of MB⁺ concentration for
forwarding the MB ionization equilibrium and transformation of the material surface from the positive (at pH <7.0) to the negative at above pH_{ZPC} (6.58). The observed results were somewhat alike to those reported by Li et al. (2016) and Pathania et al. (2017). Thus, it is confirmed that the MB adsorption on GO@IAO NC is more akin to the alkaline pH range compared to a strong acidic pH as the repulsive force between MB\(^+\) and positively charged GO@IAO NC surface is prominently operative.

**Effect of contact time**

Effect of the contact time on MB adsorption by GO@IAO was investigated taking the concentrations of MB and adsorbent 2.0 mg/L and 0.2 g/L, respectively, at 30\(^\circ\)C (303 K) and 45\(^\circ\)C (318 K) at pH 9.0 to determine the nature of reaction kinetics and rate of the reaction, which is essential for designing a large scale treatment process.

Figure 5(a) shows time dependent adsorption capacity \(q_t\) (mg/g) against the reaction time \(t\) (min). It is seen that the values of \(q_t\) increased quickly up to an initial 20 minutes of the reaction, and the extent of the \(q_t\) increase declined after 20 minutes of the reaction, indicating the gradual approach of surface saturation and almost surface saturation occurring with MB by 40–45 minutes (almost unchanged \(q_t\) value despite the increase of \(t\)). Thus the equilibrium time is ∼40–45 minutes, which is quite small in contrast to the MB adsorption over activated carbon (Pathania et al. 2017). However, the MB adsorption by GO@IAO NC is slower than that by GO but the authors loaded the MB concentration at least 62.5 times larger than the present system (Yang et al. 2011).

At the initial stages of the reaction, the majority of the active functional sites available over GO@IAO NC surface were largely utilized as the loading mass of MB per unit surface site was high, resulting in a rapid rise in \(q_t\) up to \(t = 20\) minutes and thus the rate of MB adsorption (Hameed 2009) was high. The rate slows down gradually with time owing to the diminishing of MB concentration as well as unoccupied active sites per unit area of the adsorbent surface (Chen et al. 2016). The decrease of steepness of the kinetic plot with rise of reaction temperature (Figure 5(a)) indicates a decrease of adsorption rate with temperature (Pathania et al. 2017) as the \(q_t\) values were lower at higher temperatures (45\(^\circ\)C) than lower temperatures (30\(^\circ\)C) at any contact time, indicating the exothermic nature of the MB adsorption reaction.

**Kinetic data modelling**

The kinetic data shown as points in Figure 5(a) are modelled by the non-linear least square fit method with the pseudo-first order (PFO) (Equation (3)) and the pseudo-second order (PSO) (Equation (4)) (Canzano et al. 2012) model equations:

\[
q_t = q_e \left[1 - \exp \left(-k_1 t\right)\right] \\
q_t = \frac{t \cdot k_2 \cdot q_e^2}{1 + t \cdot k_2 \cdot q_e}
\]
where $k_1$ (/min) and $k_2$ (g/mg/min) represent the PFO and the PSO rate constants, respectively. The $q_t$ and $q_e$ are MB adsorbed amount (mg.g$^{-1}$) at any time $t$ (min) and at equilibrium, respectively. The kinetic parameters related to each equation were estimated from the slope and intercept of the origin plots, which are shown in Table 1. It has been found that the experimental values of $q_t$ are nearer to the modelled $q_t$ of the PSO equation (Equation (2)) rather than the PFO equation (Equation (1)). Again, the values of regression coefficient ($R^2$) estimated were higher for the PSO equation than the PFO equation at both the temperatures, indicating that the present adsorption reaction kinetics occur in accordance with the PSO model (Pathania et al. 2017), while the kinetics of Congo red adsorption reaction with GO was of the PFO type (Debnath et al. 2014).

Thus, the MB adsorption over the GO @IAO NC surface occurred in accordance with the PSO reaction which is closely akin to the result reported by Li et al. (2016) on the removal of organic dye by Fe@C magnetic nanocapsules.

### Intra-particle diffusion kinetic modelling

The solute adsorption on any adsorbent surface may be controlled by the intra particle diffusion phenomenon (Weber & Morris 1963). Thus, the kinetic data shown as points in Figure 5(a) were analyzed using the intra-particle diffusion (IPD) model (Equation (5)) (Weber & Morris 1963) within arranged reaction times, 5–20 minutes, where values of the $q_t$ (exp) had enhanced quickly with time ($t$, minute) owing to the rapid mass transfer from solution to adsorbent surface because of the presence of high surface active sites as well as solute concentrations at that time period (Pathania et al. 2017).

$$q_t = k_d t^{0.5}$$

(5)

where $k_d$ is the IPD rate constant. The plots of the $q_t$ versus $t^{0.5}$ are shown in Figure 5(b) which shows a linear upward change of data, indicating that the boundary layer diffusion is the main component of this reaction. The $k_d$ values estimated for the working temperatures are summarized in Table 2. From the values of $k_d$, it is clear that the value of diffusion rate constant is higher at 30 °C than at 45 °C. The square term of the regression coefficient values indicate that the present adsorption process follows the diffusion rate equation perfectly in the above time frame of the reaction. The good linearity of the plot of $q_t$ with increasing $t^{0.5}$ (minute$^{0.5}$) has suggested that the MB adsorption by GO@IAO NC at the initial stages has taken place with the boundary layer diffusion process.

### Adsorption isotherm

The adsorption isotherms relate to the amount of adsorbate that can attach to the surface of the adsorbent at a definite temperature which can be used to understand the adsorption mechanism. Here, the adsorption equilibrium of MB with GO@IAO NC was investigated at temperatures of 30 °C (303 K), 45 °C (318 K) and 60 °C (333 K) allowing 45 minutes for the reaction employing dosage of GO@IAO 0.2 g/L. The values of equilibrium adsorption capacity ($q_e$, mg/g) obtained against the equilibrium concentration ($C_e$, mg/L) are presented in Figure 6. It is seen that the value of $q_e$ is found to be greater at a lower temperature than that at a higher temperature of the reaction at any given $C_e$ value, indicating the exothermic nature of the adsorption process. The data shown as points in Figure 6 were modelled by the non-linear fits of the equilibrium data with widely employed Langmuir and Freundlich isotherm equations (Canzano et al. 2012; Sharma & Das 2013) to determine the basic information of this reaction. The

<p>| Table 1 | The kinetic parameters estimated for the MB adsorption reaction with GO@IAO at pH 9.0 (concentration of MB = 2.0 mg/L, dosage of GO@IAO = 0.2 g/L and agitation speed = 300 rpm) |</p>
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pseudo-first order (PFO) $q_t - q_e[1-exp(-k_1 t)]$</th>
<th>Pseudo-second order (PSO) $q_t - t k_2 q_e^2/(1 + t k_3 q_e)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>$k_1$</td>
<td>$q_e$</td>
</tr>
<tr>
<td>30</td>
<td>0.1613</td>
<td>7.3748</td>
</tr>
<tr>
<td>45</td>
<td>0.1381</td>
<td>6.5256</td>
</tr>
</tbody>
</table>
Langmuir isotherm (Equation (6)) was developed based on the homogeneous sites for adsorption and is described as:

\[ q_e = q_m K_L C_e / (1 + K_L C_e) \]  

(6)

where \( C_e \) is the equilibrium solute concentration (mg/L), \( q_e \) is the amount (mg/g) of solute adsorbed per g of adsorbent at equilibrium, \( q_m \) and \( K_L \) are constants related to the monolayer adsorption capacity (mg/g) and the energy of adsorption (L/mg), respectively. \( q_m \) represents the monolayer adsorption capacity when the homogeneous surfaces are covered with adsorbed species having uniform energies of adsorption. The Freundlich isotherm (Equation (7)), on the other hand, was developed based on the multilayer coverage of adsorbates on heterogeneous surface and is best described as:

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

(7)

where \( K_F \) is the Freundlich adsorption capacity and \( 1/n \) is an arbitrary constant related to the adsorption intensity.

Experimental data, shown as the points, were modelled by the non-linear fit method with the isotherm equations specified earlier (Equations (6) and (7)). The related isotherm parameters estimated from the model fits of data on the origin software spreadsheet are given in Table 3, including the square of the regression coefficient (R²) and the statistical error chi-square (\( \chi^2 \)). From inspection of the model parameters, it can be said that the fits of equilibrium data are good with both the isotherms, but agreement of the data fitting with the Langmuir model (R² = 0.99) is better (Kumar & Sivanesan 2009; Gao et al. 2015) than with the Freundlich model (R² = 0.96–0.97), indicating that the adsorption sites are homogeneous, like carbon prepared from rattan sawdust (Hameed et al. 2010a) and FCBAC (Pathania et al. 2017).

However, Yang et al. (2011) reported that the equilibrium data of MB adsorption by GO abides by the Freundlich isotherm model very well (R = 0.994) indicating heterogeneity of the GO surface, while Sharma & Das (2013) suggested that the methyl green adsorption equilibrium over the GO nanosheet closely abides by the Langmuir homogeneous surface site model. The Langmuir monolayer capacity values \( q_m \) (mg/g) have been estimated to be 330.35, 313.06 and 301.55 mg/g at 303, 318 and 333 K, respectively (Table 3). Very high values of \( q_m \) indicate the prospective use of GO@IAO NC to design a filter for the treatment of MB contaminated water.

The dimensionless separation factor (\( R_L = (1 + K_L C_i)^{-1} \)), which is the special feature of the Langmuir isotherm \( (K_L = \text{Langmuir constant}, C_i = \text{initial solute concentration}) \),
should be in the range of \(0 < R_L < 1.0\) for the thermodynamically favourable adsorption process. In the case of MB adsorption by GO@IAO NC at any given temperature, it is seen that the value of \(R_L\) is less than unity even when \(C_i = 0.01\) mg/L and more than zero when \(C_i > 10^3\) mg/L of MB, suggesting thermodynamically favourable adsorption of the MB by the composite (Pathania et al. 2017).

In order to assess the efficiency of MB removal by the adsorption reaction with GO@IAO NC, the Langmuir monolayer capacity \(q_m\) (mg/g) obtained from the equilibrium studies at room temperature (303 K) was compared with the other available data (Table 4), despite the value \(q_m\) depending on the concentration range of the solute selected, pH and adsorbent dosage. Comparison of the present value of \(q_m\) with those of other materials confirms that the present material is almost equally efficient as the other carbon based material, apart from the GO (Yang et al. 2011), but is more efficient than many other non-carbonaceous materials (Table 4).

### Thermodynamics of adsorption reaction

The efficiency of an adsorption process with increasing temperature for any material can be explained by the change in standard thermodynamic parameters, such as Gibbs free energy \(\Delta G^\circ\), enthalpy \(\Delta H^\circ\), and entropy \(\Delta S^\circ\). The Gibbs free energy change of the process is related to the equilibrium constant \(K_a = \frac{1000q_e}{C_e}\) (Canzano et al. 2012; Dawood & Sen 2012) by Equations (8) and (9):

\[
\Delta G^\circ = -RT \ln K_a \tag{8}
\]

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{9}
\]

From Equations (8) and (9), we have Equation (10) as given below:

\[
\ln K_a = \left(\frac{-\Delta H^\circ}{R}\right)T^{-1} + \frac{\Delta S^\circ}{R} \tag{10}
\]

The values of \(\Delta H^\circ\) and \(\Delta S^\circ\) were calculated from the slope and the intercept of linear van 't Hoff plot \(\ln K_a\) versus \(T^{-1}\) (K) (Figure S5, available online) and are given in Table 5.

Negative values of \(\Delta G^\circ\) at the temperatures investigated have indicated the spontaneous nature of the MB adsorption reaction with GO@IAO NC (Sharma & Das 2013; Gao et al. 2015), and magnitude of the \(\Delta G^\circ\) (–26.51 to –26.61 KJ.mol\(^{-1}\)) values are nearly equal from 303 to 333 K indicating the

### Table 4 | Comparative assessment of the monolayer adsorption capacity \((q_m)\) of MB adsorption on different adsorbent

<table>
<thead>
<tr>
<th>Adsorbent material</th>
<th>(q_m) (mg/g) at 303 K</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO@IAO NC</td>
<td>330.35</td>
<td>Present work</td>
</tr>
<tr>
<td>Spent tea leaves</td>
<td>300.05</td>
<td>Hameed (2009)</td>
</tr>
<tr>
<td>Activated carbon activated with K(_2)CO(_3)</td>
<td>382.75</td>
<td>Foo &amp; Hameed (2012)</td>
</tr>
<tr>
<td>Activated carbon derived from Ficus Carica</td>
<td>47.62</td>
<td>Parthania et al. (2017)</td>
</tr>
<tr>
<td>Activated carbon from Rattan sawdust</td>
<td>294.14</td>
<td>Hameed et al. (2007a)</td>
</tr>
<tr>
<td>Magnetic polysaccharide-GO composite</td>
<td>384.4</td>
<td>Gao et al. (2015)</td>
</tr>
<tr>
<td>GO</td>
<td>714</td>
<td>Yang et al. (2011)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>400.0</td>
<td>Kumar &amp; Sivanesan (2006)</td>
</tr>
<tr>
<td>Amorphous silica</td>
<td>22.66</td>
<td>Woolard et al. (2002)</td>
</tr>
<tr>
<td>Zeolite</td>
<td>53.1</td>
<td>Dogan et al. (2000)</td>
</tr>
<tr>
<td>Fe(III)/Cr(III) hydroxide</td>
<td>22.8</td>
<td>Namasiyam &amp; Sumithra (2005)</td>
</tr>
<tr>
<td>Bentonite</td>
<td>151–175</td>
<td>Rafatullah et al. (2010)</td>
</tr>
<tr>
<td>Composite material</td>
<td>74.0</td>
<td>Vilar et al. (2007)</td>
</tr>
<tr>
<td>Fly ash</td>
<td>5.57</td>
<td>Kumar et al. (2005)</td>
</tr>
</tbody>
</table>

### Table 5 | Thermodynamic parameters for the adsorption of MB onto GO@IAO NC

<table>
<thead>
<tr>
<th>(\Delta H^\circ) (kJ/mol)</th>
<th>(\Delta S^\circ) (kJ/mol)</th>
<th>(\Delta G^\circ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>–23.38</td>
<td>0.01</td>
<td>303 K</td>
</tr>
<tr>
<td>–26.31</td>
<td>–2.66</td>
<td>318 K</td>
</tr>
<tr>
<td>–26.46</td>
<td>–2.66</td>
<td>333 K</td>
</tr>
<tr>
<td>–26.61</td>
<td>–2.66</td>
<td>333 K</td>
</tr>
</tbody>
</table>
The adsorption process is almost equally spontaneous and temperature independent. The value of entropy change ($\Delta S$) for this reaction is 0.01 kJ/mol/K (Table 5), which indicates the increase in number of species at the solid–liquid boundary layer, suggesting the increase of randomness at the interface. This is presumably due to the release of aqua molecules with adsorption of aquatic MB over the material surface. The estimated value of $\Delta H$ is 23.38 kJ/mol (less than 40 kJ/mol) which indicates the physical nature of MB adsorption by GO@IAO NC (Debnath et al. 2014). Thus, the mechanism proposed for this process can be pictorially described below (Figure 7).

**Regeneration**

Recyclability of the present material after use was checked. Here, the desorption of MB saturated material was tested successively with HCl (0.1 M), NaOH (0.1 and 0.5 M), absolute alcohol and aqueous alcohol (1:1, v/v). It has been seen that neither HCl nor NaOH can release more than 40% of adsorbed MB from the material surface. Again, the absolute or aqueous alcohol (1/1, v/v) can release 70–75% of the adsorbed MB from the solid surface when 0.1 g of the MB saturated material was agitated (10 minutes) in three successive batches with 10 mL fraction of absolute or aqueous alcohol. The better result of regeneration with alcohol is due to the higher distribution affinity of MB for the alcohol than either HCl or NaOH solution.

**CONCLUSIONS**

Graphene oxide (GO)-incorporated iron-aluminium oxide nanocomposite (GO@IAO NC) for adsorption of MB was prepared by one spot chemical precipitation from 1.0 g GO suspended 200 mL of 0.1 M mixed metal salts solution, and characterized by some modern analytical techniques. The GO@IAO NC, when used with different dosages for MB adsorption, showed the highest efficiency at lowest dosage. The adsorption of MB by GO@IAO NC increased with pH due to ionic forces between MB$^+$ ion and negative charge of the material surface (pH > pHzpc). The present adsorption reaction took place in accordance with the PSO kinetics and Langmuir isotherm. The Langmuir monolayer adsorption capacity is 330.35 mg/g at 303 K, suggesting GO@IAO NC should be a prospective material for MB removal from contaminated water. Thermodynamically, the adsorption reaction is exothermic and spontaneous. The spontaneity of the reaction is temperature independent. Absolute or aqueous alcohol (1/1, v/v) is equally good for regenerating the MB adsorbed GO@IAO up to 70–75%, indicating recyclability of the material.

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**REFERENCES**


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