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Understanding flocculation mechanism of graphene oxide for organic dyes from water: Experimental and molecular dynamics simulation

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Flocculation treatment processes play an important role in water and wastewater pretreatment. Here we investigate experimentally and theoretically the possibility of using graphene oxide (GO) as a flocculant to remove methylene blue (MB) from water. Experimental results show that GO can remove almost all MB from aqueous solutions at its optimal dosages and molecular dynamics simulations indicate that MB cations quickly congregate around GO in water. Furthermore, PIXEL energy contribution analysis reveals that most of the strong interactions between GO and MB are of a van der Waals (London dispersion) character. These results offer new insights for shedding light on the molecular mechanism of interaction between GO and organic pollutants.

I. INTRODUCTION

The textile dyeing industry adopting the wet processing technique, including dyeing, washing, printing, and fabric finishing, leads to the discharge of large quantities of wastewater containing toxic substances.1 These toxic substances contained in dyed wastewater should therefore be completely removed before being released back into the environment. Traditional techniques including adsorption, advanced oxidation processes (such as ozonation, UV/H2O2, Fenton, and ultraviolet light), electrochemical decolorization, coagulation/flocculation, membrane filtration, and biological methods,2,3 are always employed. Among these methods, coagulation and flocculation have remained being used widely for water and wastewater pretreatment.4,5 At present, inorganic metal–based flocculants and synthetic polymeric are two of the most extensively applied flocculants.5 However, since it may have severe adverse effects on human health and ecosystem that the increased concentrations of traditional flocculants in water, environmentally friendly flocculants will present an exciting alternative for the pretreatment of wastewater.

Recently, two–dimensional graphene-based material has attracted increasing interest because of its unique physicochemical properties (e.g., theoretically surface area up to 2630 m²/g, which benefits adsorption),7 and considerable studies have shown that graphene oxide (GO), an oxide form of graphene, exhibits superior adsorption capabilities for both heavy metals and various organic pollutants.8–10 Whereas, the flocculation performance of GO for organic pollutants remains unclear.
Compared with graphene and reduced graphene oxide, GO consists of more oxygen-containing groups, such as hydroxyl, carboxyl, and epoxy groups, which are beneficial to enhance dispersibility and eliminate pollutants in water. To the best of our knowledge, the available data examining the flocculation performance of GO are from an experimental study in which there is the possibility of using GO as a novel flocculant to remove kaolin, hematite, humic acid, and cationic light yellow 7GL dye, and GO can successfully remove them by sweeping effect, patching effect or charge neutralization effect. Although the flocculation mechanisms of GO were discussed in detail according to the experimental results by Yang et al., potential binding forces including van der Waals force, charge attraction, hydrogen-bonding, Lewis acid–base interaction, and π–π stacking between flocculants (for example, GO) and contaminants are still left to be understood from the view of molecular level. Recently, Chagovets et al. have modelled the methylene blue cation (MB⁺) adsorption onto the carbon nanotubes (CNT) surface by means of molecular dynamics (MD) in vacuum and in aqueous medium and have revealed the hydrophobic nature of the adsorption of the MB⁺ cation at the hydrophobic CNT surface, which is stabilized by the π–π and cation–π interactions, and by the charge transfer interaction as well. In comparison with CNT, GO has the oxygen–derived functional groups on its sheet basal plane and sheet edge, therefore, it can be proposed that stronger interactions exist between GO and MB⁺ cation. While studies addressing this question are still lacking.

In the present work, we conduct experimental studies to explore the possibility of using GO as a flocculant and simulate the adsorption of basic cationic dye MB in their natural environment (water) to GO in order to analyze binding forces between them. First, we investigate the flocculation performance of GO for MB removal under acidic, neutral and alkaline conditions, respectively, because initial solution pH can change the properties of contaminants and may affect the dissociation of functional groups contained on GO. For further comparison, we also investigate the flocculation performance of single-walled carbon nanotubes (SWCNT), a sheet of graphene rolled into a cylinder, and polyacrylamide (PAM), a traditional and popular synthetic polymeric flocculant. In the second part of the work, we carry out MD simulations for GO nanosheets interacting with MB⁺ by Material Studio using a COMPASS force field in an explicit aqueous environment. Furthermore, quantitative insights of energy contributions of intermolecular interactions between GO and MB are obtained through PIXEL method. To the best of our knowledge, researching the flocculation mechanism of GO for organic pollutants removal combining MD simulations with PIXEL method has not been reported previously, which could offer new insights for the better design of graphene-based flocculants or other wastewater pretreatment applications.

II. MATERIALS AND METHODS

A. Materials

Natural graphite powers (natural, -325 mesh) were purchased from Alfa Aesar. Single-walled carbon nanotubes (SWCNT) was purchased from Nanjing XFNANO Materials Tech Co., Ltd. MB (Sinopharm Chemical Reagent Co., Ltd.) was used without further purification, and its chemical structures and molecular sizes are shown in Fig. S1. PAM and all other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. Distilled water was used in all experiments. GO was synthesized using a modified Hummers method and the detailed preparation and characterization methods are described in Supplemental Material.

B. Flocculation tests

A stock solution of GO (1000 mg/L) was prepared by adding 100 mg of GO to 100 mL of distilled water. The stock solutions of SWCNT and PAM were also prepared. Since SWCNT cannot disperse well in water, its stock suspension was continuously stirred during the experimental period. On the basis of previous work, jar tests were then carried out to evaluate the flocculation performances of GO, SWCNT, and PAM using 250-mL jars at room temperature. Exactly 100 mL of 50 mg/L MB solution was measured into each jar test beaker. The pH levels were adjusted.
using 0.1 mol/L HCl or 0.1 mol/L NaOH aqueous solutions before addition of the flocculants. After adding designed amount of flocculants (concentration of flocculant 0–150 mg/L), the mixture was strongly stirred at a speed of 200 rpm for 5 min at the beginning, then at 50 rpm for 10 min, and finally left to settle for 1 h. After this procedure, samples solutions were collected using a syringe and filtrated by a Millipore filter with 0.45 µm pore-diameter. The residual dye concentration in the filtered water was determined by UV–visible spectrophotometry at the wavelength of 660 nm. The decoloration of MB (%) was calculated as follows:

\[
\text{Decoloration} \, (\%) = \frac{C_0 - C}{C_0} \times 100 \%
\]  

where \(C_0\) and \(C\) were the dye concentrations in the solution before and after flocculation, respectively.

C. GO structure

GO nanosheets were constructed based on the Lerf–Klinowski structural model with a molecular formula of \(\text{C}_{10}\text{O}_{1.5}\text{(OH)}_{1.5}\text{(COOH)}_{0.5}\), which represents typical outcomes from standard oxidation processes. These epoxy and hydroxyl groups are randomly distributed to the carbon atoms on a 15.74 Å × 17.43 Å graphene plane. Carboxyl groups are attached to the graphene edge as well, as shown in Fig. 1. This GO model studied here is not significantly oxidized, since it has 4 epoxy groups, 3 hydroxyl groups and 2 carboxyl groups per 116 carbon atoms. The dangling bonds at the edge of the GO model are saturated by hydrogen atoms.

D. Molecular dynamics simulations

Molecular dynamics (MD) simulations of MB cation (\(\text{MB}^+\))–GO aqueous solution are carried out in Material Studio using COMPASS force field, which is an \textit{ab initio} force field optimized for condensed-phase application. Partial charges of water, chloride ion and GO are assigned by COMPASS force field, while the partial charges of \(\text{MB}^+\) is taken from Ref. 20. A GO sheet, 5 \(\text{MB}^+\) cation (3.5 % weight) and 5 \(\text{Cl}^-\) counterions are solvated in a cubic box with 2000 water molecules.

The starting geometries of the simulation box (shown in Fig. 4(a)) are generated with the Amorphous Cell module in Material Studio. The equations of motion are integrated with a time step

![Fig. 1. Top view (top) and side view (bottom) of the energy–minimized structure of the GO sheet considered in this study: \(\text{C}_{10}\text{O}_{1.5}\text{(OH)}_{1.5}\text{(COOH)}_{0.5}\). Each sphere represents an atom using the following color rule: white, hydrogen; red, oxygen; gray, carbon.](image-url)
of 1 fs. The Nose thermostat is used to control the system at a constant temperature.\textsuperscript{21} The pressure is maintained constant with Berendsen barostat.\textsuperscript{22} Periodic boundary conditions are applied, and the simulations are conducted using the NPT ensemble with a constant pressure of 1 bar and constant temperature of 298 K. Van der Waals interactions are treated with a cutoff distance of 12.5 Å and long-range electrostatic interactions are treated using the particle–particle/particle–mesh (PPPM) method.\textsuperscript{23} The trajectories, velocities and forces corresponding to all atoms in the system are saved in every 2 ps.

### III. RESULTS AND DISCUSSION

#### A. Characterization of flocculants

The layered nature of GO was demonstrated via scanning electron microscopy (SEM) and transmission electron microscopy (TEM), which shows the GO sheets are composed of thinner layers with some wrinkles (Fig. S2\textsuperscript{33}), implying fine flexibility in the GO sheets. Different functional groups are found in the Fourier transform infrared (FTIR) spectrum of GO (Fig. S3\textsuperscript{33}), that is, C=O group at 1736 cm\textsuperscript{-1}, C=C at 1622 cm\textsuperscript{-1}, epoxy C–O group at 1220 cm\textsuperscript{-1} and primary C–OH group at 1038 cm\textsuperscript{-1}, indicating the existence of large amounts of oxygen-containing functional groups on GO nanosheets.\textsuperscript{24} In the X–ray diffraction (XRD) pattern (Fig. S4a\textsuperscript{33}), the peak at \(2\theta = 10.7^\circ\) indicates that the interlayer spacing of GO is 8.2 Å, which is similar to the findings of previous studies.\textsuperscript{25} The Raman spectrum (Fig. S4b\textsuperscript{33}) of GO shows the typical D peak (1355 cm\textsuperscript{-1}), G peak (1589 cm\textsuperscript{-1}) with an \(I_D/I_G\) intensity ratio of 0.96, confirming lattice distortions induced by oxidation.\textsuperscript{26} All these characterization results confirm that GO has been prepared successfully.

#### B. Flocculation studies

The flocculation performance of GO was investigated, and SWCNT and PAM were also tested as comparison. The initial evaluation of the flocculation process was determined by analysis of MB removal efficiencies. The flocculation performance of flocculants for MB was studied at different dosages and various pH levels because many recent studies\textsuperscript{5,6} have shown that flocculants dosage and pH are two of the most important external factors and the results are shown in Fig. 2. An overview of the figures shows that all the three flocculants are able to remove MB to a certain extent. Their optimal dosages and residual contaminant percentages under various pH levels are summarized in Table S1.\textsuperscript{33} However, GO exhibits higher efficiency than the other two for the flocculation of MB, which agrees with the results reported by Yang et al.\textsuperscript{6} Moreover, GO can remove almost all MB from aqueous solutions under consuming lower optimal dosages at any pH (see Fig. 2 and Table S1\textsuperscript{33}). This is due to the strong interaction between GO and MB as described in detail in the next section. By contrast, SWCNT always displays the worst performance among the three flocculants under any pH condition. This may be attributed to the fact that SWCNT has poor dispersibility,\textsuperscript{5} resulting in very weak interaction between SWCNT and MB, which is in accordance with a recent experimental study by Simate et al.,\textsuperscript{5} who also found that pristine CNT performed worse than acid functionalized CNT and Ferric chloride (a inorganic flocculant). As for PAM, little flocculation ability for MB can presumably be explained by the fact that soluble contaminants enhance the difficulty of flocculation.\textsuperscript{6}

The further evaluation was determined by observation of floc properties as they are of great importance for water treatment.\textsuperscript{27} The images were shown in Fig. S5.\textsuperscript{33} During flocculation process, GO quickly produces visible flocs when it contacts with MB solutions under any pH conditions (Fig. S5a\textsuperscript{33}). When the dosage of GO is low (20 mg/L and 40 mg/L), the structure of the flocs is small granular (Fig. S6a\textsuperscript{33}). With the increase of dosages of GO, it produces larger and denser flocs (Fig. S6a\textsuperscript{33}), which is more favored in further sludge handling. This result indicates that GO can destabilize MB molecular efficiently to produce larger aggregates through the strong interaction between GO and MB molecular or/and by the sweeping effect.\textsuperscript{5} By contrast, PAM yields very few
flocs (Fig. S5b and S6b) and no obvious floc is observed when applying SWCNT as flocculant (Images not shown).

C. Flocculation mechanism

It is widely agreed that six possible interactions including hydrophobic effect, $\pi - \pi$ bonds, hydrogen bonds, covalent, electrostatic interactions and van der Waals force have been observed and are responsible for the interactions of organic chemicals on carbon nanomaterials (CNMs) surface. Among these forces, van der Waals force is normally the dominant force for attractions between atoms, molecules, and surfaces. Hydrogen bonding interaction and covalent bonds can form and play a pivotal role in adsorption when the organic chemicals and CNMs have certain functional groups such as $-\text{COOH}$, $-\text{OH}$, and $-\text{NH}_2$. $\pi - \pi$ bonding interaction has been used to interpret the adsorption of organic molecules with a C=C double bond or a benzene ring on the surface of CNMs because these organic molecules contain $\pi$ electrons to interact with the $\pi$ electrons of the benzene rings on CNMs surface through the $\pi - \pi$ electron coupling. Electrostatic attraction will occur if CNMs and organic chemicals have opposite charges; otherwise, electrostatic repulsion will occur if both CNMs and organic chemicals have the same sign of charges. As for hydrophobic interaction, it can only been employed to interpret the adsorption of hydrophobic organic chemicals by CNMs. In this study, MB is a hydrophilic dye and we can see that it does not have certain functional groups such as $-\text{COOH}$, $-\text{OH}$, and $-\text{NH}_2$ from its chemical structure (Fig. S1). So these three interactions (that is hydrophobic effect, hydrogen bonds, and covalent interaction) are not responsible for the interaction between GO and MB molecular. In order to understand the charge interaction between GO and MB, we carried out zeta potential of GO at various pH (Fig. S7). Similar to previous reports, the zeta potential of GO was negative within the pH studied. Accordingly, the electrostatic attraction may occur when GO contacts with cationic MB$^+$. In addition, as GO is a functionalized graphene with oxygenated groups (e.g., $-\text{COOH}$, $-\text{OH}$, $-\text{C}=\text{O}$) on its structure, particularly those synthesized via Hummers procedure, we speculate that van der Waals force, electrostatic interactions, and $\pi - \pi$ bonds may be responsible for the interaction between GO and MB molecular. Many previous studies have also speculated that the electrostatic attraction and $\pi - \pi$ bonds could be involved in the adsorption of MB on GO.
FIG. 3. Representative simulated trajectories of adsorption of methylene blue cations on graphene oxide in aqueous solution. Water is shown in (a) and not shown for clarity in (b–h). Each sphere represents an atom using the following color rule: white, hydrogen; red, oxygen; gray, carbon; blue, nitrogen; yellow, sulfur; green, chloride. The graphene oxide is shown as grey–bonded sheet, while methylene blue cations are shown as larger spheres.

D. Molecular dynamics simulations

To understand the underlying molecular mechanism of the flocculation GO for MB, we performed MD simulations to study the detailed interactions of GO with MB$^+$. First, the entire system is energy-minimized. At the beginning of the simulation, GO and MB$^+$ are randomly placed in the water box, shown in Fig. 3(a)–3(b). Then, a 6 ns NPT molecular dynamics trajectory is generated to study the interaction of GO and MB$^+$ in aqueous solution. MB$^+$ ions gradually gather around GO during the simulation, shown in Fig. 3(c)–3(h). It takes only 2 ns for all the MB$^+$ ions adsorbed on GO (Movie S1$^{13}$).

To obtain quantitative insights about the adsorption process, we further analyzed both the physical interactions and average distance between the GO and MB$^+$. Figure 4 shows the variation of the average GO–MB$^+$ distance as a function of time, together with the interaction energy profiles between GO and MB$^+$ cations. At 0 ns, the position of GO and MB$^+$ cations are randomly assigned and the GO-MB$^+$ distance is relatively large, i.e. around 20 Å, shown in Fig. 3(b). Figure 3(c) shows that one MB$^+$ cation is adsorbed on GO at 0.5 ns. Correspondingly, the average GO–MB$^+$ distance

FIG. 4. Time evolution of the average GO–MB$^+$ distance (in black) and the interaction energy between GO and MB$^+$ cations (in red). The average GO–MB$^+$ distance is the average distance between the center of mass (COM) of GO and COM of MB$^+$ cations.
Atoms on the GO are selected (highlighted in yellow) when its distance from the MB$^+$ cations is less than 5.5 Å.

**TABLE I.** Energy contributions of intermolecular interactions between GO and MB.

| Energy type$^a$ | $E_{\text{Coul}}$ | $E_{\text{Pol}}$ | $E_{\text{Disp}}$ | $E_{\text{Rep}}$ | $E_{\text{Tot}}$ |
|-----------------|------------------|------------------|------------------|------------------|------------------|
| Energy (kJ/mol) | -36.0            | -46.2            | -80.0            | 53.7             | -108.5           |

$^a$ $E_{\text{Coul}}$, $E_{\text{Pol}}$, $E_{\text{Disp}}$, $E_{\text{Rep}}$, and $E_{\text{Tot}}$ represent coulombic, polarization, dispersion (van der Waals), repulsion and total energy, respectively.

decreases to around 18 Å and the magnitude of interaction energy increases from 2.5 kcal/mol to 25.5 kcal/mol. Subsequently, more MB$^+$ cations gather around GO. The GO–MB$^+$ distance is gradually decreasing and the magnitude of interaction energy is growing, until the system reaches equilibrium at about 2 ns. After equilibration, the average GO–MB$^+$ distance is around 10 Å.

To obtain quantitative insights into energy contribution of intermolecular interactions between GO and MB$^+$ cation, PIXEL energy calculation is conducted by PIXELD module in CLP computer program package (version 12.5.2014). The PIXEL method is preferred, since the total interaction energy can be partitioned into their coulombic, polarization, dispersion and repulsion parts, shedding light on the nature of intermolecular interactions leading towards the flocculation. The configuration of GO and one of the MB cations in the system at 6 ns (shown in Fig. 5) is chosen to analyze the contributions of interaction energy. One limitation of the CLP package is that only molecules with less than 100 atoms are able to be analyzed. Thus, GO should be trimmed based on a distance criteria. Here, atoms on the GO are considered when their distance from the MB cation is less than 5.5 Å, shown in Fig. 5. Dangling carbon and oxygen atoms at the edge of the trimmed GO are deleted to generate reasonable GO structure. In order to guarantee a rational simplified trimmed GO, we compare the interaction energy (calculated with COMPASS force field$^{14}$) between GO and MB cation with that of between trimmed GO and MB. Only 3.37 % difference is observed in the interaction energy of two systems, indicating that it is reasonable to employ the trimmed GO to study the energy distribution between trimmed GO and MB. Geometry optimization of the trimmed GO with 86 atoms and MB are performed at the B3LYP/631 level$^{31}$ using Gaussian package.$^{32}$ The molecular electron densities are calculated with Gaussian at the same level as the input for the PIXEL energy calculations. The PIXEL energies are listed in Table I, indicating that London dispersion energy (van der Waals energy) dominates the interaction energy.

**IV. CONCLUSIONS**

In summary, GO exhibits higher efficiency than SWCNT and PAM for the flocculation of MB and enjoys lower optimal dosages at any pH studied. Moreover, GO can remove almost all MB from aqueous solutions due to the strong interaction between GO and MB molecular. PIXEL energy calculations first reveal that London dispersion force is the dominant force for the interaction, indicating the electrostatic interaction and other noncovalent interactions between MB$^+$ and GO are
weak, as opposed to the previous speculations\textsuperscript{8,29,30} that the electrostatic attraction may be responsible for the interaction between GO and MB molecular. Thus, our findings are able to provide implications for better understanding the molecular mechanism of interaction of GO with organic pollutants especially for those cationic organic compounds.

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33. See supplementary material at http://dx.doi.org/10.1063/1.4936846 for detailed methods on the preparation procedures and characterization methods of GO; chemical structures and molecular sizes of MB calculated from the software of Chem3D Pro 14.0 using the Minimize Energy function (Fig. S1); SEM (top) and TEM (bottom) images of graphite (a) and GO (b) (Fig. S2); FTIR spectra of graphite and GO (Fig. S3); XRD (a) and Raman (b) spectra of GO (Fig. S4); photos of the flocculation performances of GO (a) and PAM (b) for MB removal from aqueous solutions (Fig. S5); photos of the structure of the flocs. (a) GO; (b) PAM (Fig. S6); Zeta potential-pH profiles of GO (Fig. S7); the flocculation performance of GO and PAM at different pH conditions for MB removal (Table S1); and a 6 ns NPT molecular dynamics video on the interaction of GO and MB$^{+}$ in aqueous solution (Movie S1).