Rapid Synthesis of Porous Graphene Microspheres through a Three-Dimensionally Printed Inkjet Nozzle for Selective Pollutant Removal from Water

Dawei Li,† Hao Zhang,‡ Li Zhang,† Panfeng Wang,† Hong Xu,*† and Jin Xuan*†‡

1State Key Laboratory of Chemical Engineering, School of Mechanical and Power Engineering, East China University of Science and Technology, 200237 Shanghai, China
2Department of Chemical Engineering, Loughborough University, LE11 3TU Loughborough, U.K.

ABSTRACT: Graphene microspheres are fabricated through a 3D-printed inkjet nozzle based on the gas–liquid microfluidic method. This method realizes rapid and controllable fabrication of uniform graphene microspheres with up to 800 μL min⁻¹ (ca. 1 L d⁻¹) of yields, which is 2 orders of magnitude higher than those of the conventional microfluidic method. The diameter of the graphene microspheres could be flexibly controlled from 0.5 to 3.5 mm by adjusting the gas pressure. The porous graphene microspheres show great dye decoloration performance. The maximum adsorption capacity of methylene blue is 596 mg/g, which is the highest adsorption capacity among that of the reduced graphene-oxide absorbents. A performance improvement of 21% is obtained by applying sodium alginate into graphene as a curing agent. The adsorption behavior follows a Langmuir isotherm and pseudo-second-order kinetic model. Besides, the graphene microspheres exhibit great selective adsorption and could separate cationic dye methylene blue (MB) and anionic dye methyl orange (MO).

1. INTRODUCTION

The shortage of freshwater resources is a global environmental issue. Water contamination caused by the development of industry and human activities is consuming the freshwater resource severely.¹⁻¹² Pollutants in water lead to a great threat on the environment and ecosystem.¹³⁻¹⁶ Organic pollutants, such as dyes, antibiotics, and pesticides, and heavy-metal ions such as Cu²⁺, Pb²⁺, Hg²⁺, and Cr⁶⁺ are considered as the most serious contaminants.⁵,⁶ Physical adsorption is regarded as a promising way for the removal of those hazardous pollutants.⁴ Graphene and its derivatives have been gaining intensive research interest in water treatment application due to their great specific surface areas and excellent adsorption performance.⁷⁻⁸ Besides, graphene is regarded as a promising support for photocatalysts such as TiO₂ and ZnO for in situ degradation of adsorbed organic contaminants.⁹,¹⁰

Although many research works on developing 2D graphene-based absorbents have been carried out,¹¹⁻¹² the irreversible re-stacking and agglomeration of graphene caused by the van der Waals forces and π–π bonds between graphene layers severely reduce the number of active adsorption sites thus resulting in inevitable performance degradation. Moreover, the suspended 2D graphene is difficult to retrieve and regenerate. In order to improve the retrieval performance and maintain the large surface area of graphene at the same time, porous graphene with a 3D geometric structure is desirable,¹³⁻¹⁶ such as graphene films, graphene tissues, graphene sponges, and graphene spheres.¹⁷,¹⁸ The 3D geometric structure of graphene could be fabricated by various methods, including self-assembly,¹⁹⁻²¹ additive manufacturing, sol–gel methods,²¹ electrostatic spinning,²² and microfluidics.²³⁻²⁵ Ma et al.²⁵ fabricated porous graphene gels based on a combined sol–gel and hydrothermal method for methylene blue (MB) adsorption. An adsorption capacity as high as 192 mg/g of the ultralight reduced-graphene oxide gels is achieved. Nevertheless, the traditional self-assembly and sol–gel method are limited by the volume of the reactor, which restricts the continuous production of graphene.²⁶⁻²⁸ Electrostatic spinning could be used to fabricate graphene microspheres, but the diameters of the product are highly nonuniform.²⁹ Additive manufacturing, also known as 3D printing, holds bright prospects in producing graphene in complex geometric structures. Zhu et al.³⁰ demonstrated a 3D graphene aerogel fabricated through the 3D-printing method, which exhibits a great surface area and high compressibility. However, it is inefficient and high in cost to achieve mass production of 3D-geometric graphene through additive manufacturing. As for microfluidic methods, shearing forces between flowing immiscible phases are used to pellet evenly dispersed graphene particles. Benefiting from continuous operation and excellent
shape controlling, the microfluidic approach holds promise on the continuous production of 3D graphene on an industrial scale. Wang et al.31 produced well-shaped 3D graphene microspheres with a uniform size by microfluidics, which exhibit high adsorption activity against organic and inorganic contaminants. To the best of our knowledge, all types of microfluidic generation of 3D-geometric graphene are based on a liquid−liquid two-phase flow in which organic solutions such as n-hexane and silicon oil20,21 are used as the continuous phase. In liquid−liquid microfluidics, low flow rates have to be kept (generally less than 200 mm s−1) to maintain the droplet flow pattern. As a result, the yield of graphene products is restricted by the operation flow rates. The design and manufacturing of microfluidic chips are other crucial factors affecting the production of 3D-geometric graphene. The commonly applied method for microfluidic chip fabrication includes glass capillary assembly, etched silicon assembly, and soft lithography.32−34 The processes of these methods are complex and not suitable for the fabrication of sophisticated flow structures, which is necessary for preparing special structures like shell or core−shell geometries.

To fill the gap, this study aims to develop a novel rapid synthesis method with higher production rates in orders of magnitude for 3D ultralight graphene aerosol microspheres with highly porous microstructures. In order to achieve a higher yield of microspheres, an air−liquid shearing flow rather than a conventional liquid−liquid process was applied. Because of the replacement of the liquid shear phase by air, a higher flow rate of the continuous phase could easily be achieved due to the higher dispersion-phase flow rate. A 3D nozzle embedded with microfluidic channels was designed and fabricated via 3D printing to realize the air−liquid-based fast manufacturing process. The structure of the 3D nozzle and the sketch map of microsphere fabrication are shown in Figure 1a,b. The yield of shaped microspheres reaches 800 μL min−1 (ca. 1.1 L d−1), compared to 2 μL min−1 (ca. 3 mL d−1) from conventional liquid−liquid methods.31 The diameter of microspheres can be easily manipulated by adjusting the flow rates of air and gel. The porous structure of the 3D graphene microspheres is formed and controlled by using sodium alginate (SA) as the curing agent.35 The calcium alginate (CA) generated by SA works as a framework of microspheres, and the ice formed in lyophilization works as a pore template.36 Taking methylene blue as a target contaminant, the adsorption capacity of the microspheres is 596 mg g−1, which is among the highest adsorption capacities compared in reported graphene
adsorbents. In addition, the prepared materials show great selective adsorption of cationic over anionic pollutants.

2. RESULTS AND DISCUSSION

2.1. Droplet Formation Dynamics. The formation of droplets could be divided into four stages, as shown in Figure 2a. First, the size of the droplet increases with the ink jetting followed by the necking stage when the droplet keeps growing. In the third stage, the droplet falls off when reaching the force balance. Finally, the droplet becomes a sphere under the surface tension. The time interval of droplet formation is 290 ms when the inlet pressure is 0.020 MPa, and the flow rate is 200 μL min⁻¹. Figure 2b shows the relationship between inlet pressure and the diameter of microspheres. The diameter of microspheres decreases with the increment of inlet pressure. Our previous study has demonstrated that the oxides increase the surface tension of the ink.37 As a result, the diameter could be tuned from 0.5 to 3.5 mm. Benefiting from the low viscosity of the continuous phase (air), the fabrication of microspheres can be operated at a higher flow rate, which could achieve the rapid fabrication of graphene microspheres. The maximum flow rate of the ink phase (i.e., the production yield of 3D graphene microspheres) can reach 800 μL min⁻¹. For comparison, the flow rate of the traditional liquid-liquid microfluidic method is only 2 μL min⁻¹.31

2.2. Material Characterization. The X-ray diffraction patterns of the GM, GB, and GO are shown in Figure 3a to give the crystal information of these samples. The peak at 10° of GO corresponds to the typical peak of GO, and it relates to the (001) reflection of graphite oxides. The peaks at 25° in patterns of GM and GB are related to the (002) crystalline plane of carbon (JCPDS no. 26-1077).38 Raman spectra in Figure 3b show the structure information of the GM and GB. Two remarkable peaks show in the spectra of both samples. The peaks at 1593 and 1352 cm⁻¹ of the GM are assigned to the G band and D band. The G band is a typical feature of graphene, which is related to the stretching vibration of sp² carbon atoms. The D band is caused by the defects and functional groups in the graphene structure.59 The D band and G band of GB samples are at 1357 and 1592 cm⁻¹. There is no noticeable shift of peaks, thus it could be concluded that the GM and GB samples have the same graphene structure.

Figure 4 shows the morphology and porosity microstructure of the GM and GB. The fabricated microspheres are found to be well-shaped with an average diameter of 1 mm (Figure 4a,b). A highly porous sponge microstructure is detected within GMs. The pore size is in the magnitude of 10⁻⁶ m. The picture and microstructure images of the original GB are shown in Figure 4c,d as well. The results indicate that no morphology change is observed between the GM and GB. Figure 5a shows the results of nitrogen adsorption/desorption isotherms and pore size distribution. The calculated specific surface areas through the BET model for the GM and GB are 159 and 206 m² g⁻¹, respectively. It could be figured out that, the N₂ adsorption-desorption isotherm curves for both GMs and GB show the feature of type-IV isotherms with hysteresis loops with a relative pressure between 0.45 and 1.0, which indicates that both materials are mesoporous.

The size distribution of mesopores calculated by the BJH method is presented in Figure 5a. The average pore size of the GM is 8.0 nm, and the pore volume is 0.3196 cm³ g⁻¹. Meanwhile, the average pore size of GB is 10.9 nm, and the pore volume is 0.5780 cm³ g⁻¹. It can be found that the surface area of GB is lightly higher than that of GMs, while the average pore size and pore volume of GMs are smaller than the ones of GB. This is attributed to the fact that the surface area of calcium alginate is smaller than that of graphene.
hand, the calcium alginate framework shrank during the hydrothermal treatment, which could lead to a decrease in the volume of graphene microspheres and therefore the reduction in the pore size and pore volume as well.

Figure 5b gives the results of the differential thermal gravity (DTG) analysis for various samples fabricated. It is found that the graphene oxides (GOs) experience two weightloss stages. The first stage occurs from 150 to 250 °C, which can be attributed to the surface oxygen-containing functional group being oxidized. Meanwhile, the second stage is recorded from 510 to 660 °C, owing to graphene oxidization. For the GM, two stages of weightloss are also detected. The weight loss between 390 and 490 °C is attributed to the oxidation of calcium alginate, resulting in the loss of oxygen-containing functional groups on its surface. The weightloss from 490 to 680 °C is attributed to graphene oxidization. In contrast, GB shows a different DTG characterization with only one stage, that is, 490 to 700 °C, caused by graphene oxidization.

FTIR spectrograms are shown in Figure 6 to help understand the surface functional groups of the samples. The peaks at 3430 cm$^{-1}$ are attributed to −OH stretching vibration, and the peaks at 1623 cm$^{-1}$ mark the C==C skeletal stretching vibration. The peaks at 1730 cm$^{-1}$ are assigned to C==O stretching vibration, and peaks at 1413 cm$^{-1}$ are ascribed to O==C−O stretching vibration. Peaks at 1225 cm$^{-1}$ mark C−OH stretching vibration. Peaks at 1114 cm$^{-1}$ correspond to C−O stretching vibration. Peaks at 600 cm$^{-1}$ reflect the C−H bending vibration. It is obvious that the oxygen-containing functional groups of GB and GM samples are less than those of the GO sample. It is because the carbonyl and hydroxy groups on the GO surface are reduced by hydrothermal treatment. The existence of abundant oxygen-containing functional groups indicates that the three samples are negatively charged on the surface, which is profiical for the dye adsorption. Besides, the results indicate that the GM sample shows almost the same peaks with the GB sample, which means the species of oxygen-containing functional groups of the GM and GB are similar. It is also concluded that the addition of the template does not change the surface functional groups on the graphene material. It should be noted that the peak intensities of the GM sample are higher than those of the GB sample, which indicated that the amount of oxygen-containing functional groups on the surface of the GM is larger than that of GB. The oxygen-containing functional groups are believed to play a crucial role in decolorating.

2.3. Adsorption Performance. To investigate the selective adsorption performance of GMs and GB for cationic and anionic pollutants, cationic methylene blue (MB) and anionic methyl orange (MO) are chosen as target contaminants. Figure 7a shows the effect of the initial concentration of contaminants on adsorption performance. It can be found that the adsorption capacities for both MO and MB increase along with the initial concentration and reach a plateau at approximately 300 mg L$^{-1}$. The maximum adsorption capacity of GM is 596 mg/g for MB and 65 mg/g for MO. The adsorption capacity of MB microspheres is 13% higher than that of the graphene sponge reported in the literature (526 mg g$^{-1}$), which is among the highest adsorption capacities for 3D-geometric graphene adsorbents. As for GB, the maximum adsorption capacities for MB and MO are 492 and 170 mg g$^{-1}$, respectively. The results show that the adsorption capacity of GMs for MB is 21% higher than that of GB. This is attributed to the addition of SA, which could introduce the favorable oxygen-containing functional groups for MB adsorption. Beyond that, the GM sample shows great selective adsorption properties. Herein, a ratio of adsorption capacities for MB and MO, that is, $R$, is defined to clarify the selective performance of the graphene-based material as shown in eq 1.

$$R = \frac{Q_{MB,\text{max}}}{Q_{MO,\text{max}}}$$  (1)
The values of $R$ for GMs and GB are 9.15 and 2.89, respectively. Furthermore, Figure 7b shows the separated adsorption results. Comparing with GB, the GM exhibits a much higher MB removal capacity. After the treatment of the GM, the major contaminant left in the solution is MO. Meanwhile, both MB and MO exist in the solution after the treatment of GB. The results prove the unique selective adsorption property of GMs.

It should also be noticed that the selective adsorption performance has been intensified remarkably benefiting from the addition of SA. The reason for the excellent adsorption and selectivity property could be explained by the electrostatic interaction of $\pi-\pi$ bonds and surface functional groups. The $\pi-\pi$ bonds are the major interaction force, which is abundant in the graphene planar structure. Otherwise, the C=O/O--C=O bonds are also favorable for MB adsorption due to their negative-charge nature. As discussed in Section 2.3, the FTIR spectrum shows that the amounts of $\pi-\pi$ bonds and oxygen-containing functional groups on the GM surface are higher than those on the GB sample, which result in the improvement of the adsorption capacity of MB. This is because the O=C=O and -OH bonds on the chain structure of SA were introduced in the GM. However, it is notable that the -OH bonds do not contribute to the MB adsorption due to the steric hindrance. As a result, the adsorption performance of graphene microspheres is mainly attributed to C=O and O--C=O groups. Likewise, the negative-charge nature of C=O/O--C=O bonds on the GM shows repulsion to MO adsorption. Thus, the GM presents a highly selective adsorption performance.

**2.4. Adsorption Isotherm Modeling.** The adsorption isotherms of MB via GMs and GB are shown in Figure 8. The adsorption isotherm is used to reveal the bond mode of the target molecule and absorbent. The equilibrium adsorption parameters are modeled with the Langmuir and Freundlich isotherm models. The Langmuir isotherm model describes an adsorption process that the target molecule occupies only one adsorption site, which is abundant in the graphene planar structure. Otherwise, the C=O/O--C=O bonds are also favorable for MB adsorption due to their negative-charge nature. As discussed in Section 2.3, the FTIR spectrum shows that the amounts of $\pi-\pi$ bonds and oxygen-containing functional groups on the GM surface are higher than those on the GB sample, which result in the improvement of the adsorption capacity of MB. This is because the O=C=O and -OH bonds on the chain structure of SA were introduced in the GM. However, it is notable that the -OH bonds do not contribute to the MB adsorption due to the steric hindrance. As a result, the adsorption performance of graphene microspheres is mainly attributed to C=O and O--C=O groups. Likewise, the negative-charge nature of C=O/O--C=O bonds on the GM shows repulsion to MO adsorption. Thus, the GM presents a highly selective adsorption performance.

**Table 1. Langmuir and Freundlich Isotherm Parameters of MB Adsorption on Graphene**

| graphene | $T$ (K) | $Q_m$ (mg g$^{-1}$) | $K_L$ (L mg$^{-1}$) | $R^2_L$ | $R^2$ | $K_F$ | $n$ | $R^2$ |
|----------|--------|---------------------|---------------------|--------|-------|------|------|-------|
| GM       | 298    | 595                 | 0.178               | 0.9989 | 0.0111–0.2809 | 343.95 | 10.66 | 0.9119 |
| GB       | 298    | 488                 | 0.301               | 0.9985 | 0.0066–0.1425 | 340.17 | 15.2  | 0.9770 |

The adsorption isotherms of MB via GMs and GB are shown in Figure 8. The adsorption isotherm is used to reveal the bond mode of the target molecule and absorbent. The equilibrium adsorption parameters are modeled with the Langmuir and Freundlich isotherm models. As discussed in Section 2.3, the FTIR spectrum shows that the amounts of $\pi-\pi$ bonds and oxygen-containing functional groups on the GM surface are higher than those on the GB sample, which result in the improvement of the adsorption capacity of MB. This is because the O=C=O and -OH bonds on the chain structure of SA were introduced in the GM. However, it is notable that the -OH bonds do not contribute to the MB adsorption due to the steric hindrance. As a result, the adsorption performance of graphene microspheres is mainly attributed to C=O and O--C=O groups. Likewise, the negative-charge nature of C=O/O--C=O bonds on the GM shows repulsion to MO adsorption. Thus, the GM presents a highly selective adsorption performance.
site, and the adsorption sites are homogeneous on the adsorbent surface.\textsuperscript{52} The linear equation of the Langmuir isotherm model is shown in eq 2 as follows.

\[
\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m}
\]

(2)

where \(C_e\) is the concentration of equilibrium (mg L\(^{-1}\)), \(Q_e\) is the capacity of equilibrium (mg g\(^{-1}\)), \(Q_m\) is the maximum capacity (mg g\(^{-1}\)), and \(K_L\) is the Langmuir constant (L mg\(^{-1}\)). The fitting results of the Langmuir isotherm model are shown in Figure 8a, and the parameters are listed in Table 1.

The Freundlich isotherm model expresses the heterogeneous adsorption process, which assumes that the multilayer adsorption occurs on the absorbent surface. The linear equation of the Freundlich isotherm model is given in eq 3.

\[
\ln Q_e = \ln K_F + \frac{\ln C_e}{n}
\]

(3)

where \(Q_e\) is the capacity of equilibrium (mg g\(^{-1}\)), \(C_e\) is the concentration of equilibrium (mg L\(^{-1}\)), and \(K_F\) (L mg\(^{-1}\)) and \(n\) are the Freundlich constants, which relate to the adsorption capacities and favorable adsorption process.\textsuperscript{53} The fitting results of the Langmuir isotherm model are shown in Figure 8b, and the parameters are listed in Table 1. It is found that the adsorption process of GB follows the Langmuir isotherm model with the regression coefficient \(R^2\) of Langmuir being 0.999 and 0.999, compared to the ones of the Freundlich isotherm model, 0.912 and 0.977. The results indicate that the active sites on the surface of the graphene microsphere and graphene bulk are uniform, and the MB molecules are adsorbed homogeneously. It can be also confirmed that the adsorption of MB on the surface of absorbents is monolayer adsorption.\textsuperscript{54} The maximum adsorption capacities of MB calculated via the slope of the Langmuir fitting model are 595 and 488 mg g\(^{-1}\), which match well with the experimental data. In addition, another critical parameter of the Langmuir isotherm model is the dimensionless constant separation factor (\(R_L\)), which can be calculated by eq 4, which is used to describe the adsorption process. The adsorption process is normally considered effective when \(R_L\) is between 0 and 1.\textsuperscript{55}

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

(4)

where \(K_L\) is the Langmuir constant (L mg\(^{-1}\)) and \(C_0\) is the initial concentration of MB solution (mg L\(^{-1}\)). The calculation results are recorded in Table 1. The \(R_L\) value of the GM is in the range of 0.0111–0.2809, and that of GB is in the range of 0.0066–0.1425. The \(R_L\) values of both absorbents are between 0 and 1, which suggested that the absorbents are favorable for adsorption of the MB dye.

2.5. Adsorption Kinetics. In order to give more insights on the adsorption process, batch adsorption experiments are carried out for adsorption kinetics and mechanism analysis. The influence of contact time is displayed in Figure 9a. The adsorption capacity increases sharply before 90 min, but from 90 to 400 min, the adsorption speed decreases. The adsorption capacity almost reaches a maximum value at 400 min. The decoloration process is also displayed in Figure 9a. To analyze...
The adsorption kinetics, the pseudo-first-order model (eq 5) and pseudo-second-order model (eq 6) are applied to fit the kinetics data. \(^{25,56}\)

Pseudo-first-order model:
\[
\log(Q_e - Q_t) = \log Q_e - \frac{k_1 t}{2.303}
\]  
(5)

Pseudo-second-order model:
\[
\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2}
\]  
(6)

where \(Q_e (\text{mg g}^{-1})\) is the capacity of equilibrium, \(t\) is the contacting time (min), \(Q_t (\text{mg g}^{-1})\) is the capacity at \(t\) min, and \(k_1\) and \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) are the pseudo-first-order model and the pseudo-second-order model constants, respectively.

The fitting results are shown in Figure 9b,c, and the kinetic parameters are listed in Table 2. The results suggested that the adsorption process follows the pseudo-second-order model. Moreover, the calculated equilibrium adsorption capacity (319 mg g\(^{-1}\)) is closer to the experimental value (306 mg g\(^{-1}\)).

In order to describe the MB diffusion mechanism, the intraparticle diffusion model is adapted to fit the adsorption process data. \(^{57}\) The intraparticle diffusion model is given in eq 7 as follows.
\[
Q_t = k_p t^{1/2} + C
\]  
(7)

where \(Q_t (\text{mg g}^{-1})\) is the capacity at \(t\) min, \(k_p\) is the intraparticle diffusion model rate constant, and \(C\) is the intercept, which shows the thickness of the boundary layer. The linear fitting curve is shown in Figure 9d, and the fitting parameters of the intraparticle diffusion model are presented in Table 3. The process can be divided into two stages. \(^{36}\) In the first stage, the slope is higher than in the second stage, which suggests a faster MB adsorption in this stage. On the other hand, the intercept \(C\) does not equal to 0, which indicates that the diffusion process is determined by not only intraparticle diffusion but also other processes such as boundary-layer adsorption and surface adsorption. \(^{38}\) With the occupation of active adsorption sites, the adsorption speed slows down. In the second stage, the diffusion process enters a gradual stage. The MB molecules almost occupy all active sites, and the adsorption process reaches equilibrium.

The adsorption–desorption experiments were carried out to test the recyclability performance of the GM. Five milligrams of GM was added into a 20 mL MB solution of 200 mg L\(^{-1}\). As shown in Figure 10, the absorption performance decreases along with the number of cycles and remains at 25.2% after five regeneration cycles.

3. CONCLUSIONS

The graphene microsphere with a 3D porous structure is rapidly fabricated through a gas–liquid based microfluidic method, and the diameter of the microsphere can be easily tuned by gas pressure. The yield can reach up to 800 μL min\(^{-1}\), which is far beyond the yield of the liquid–liquid method (1–2 μL min\(^{-1}\)), and the morphology is stable and uniform. The GM shows great adsorption properties. The maximum capacity for MB of GMs is 596 mg g\(^{-1}\), which is almost 21% higher than that of graphene (GB) reduced by a traditional hydrothermal method with VC. It is also found that MB presents the highest adsorption performance in the reduced graphene oxides’ adsorption research. On the other hand, the capacity for MO is 65 mg g\(^{-1}\), which is 62% lower than that of graphene (GB) reduced by the traditional hydrothermal method with VC. The selectivity reflects in the different values of adsorption of anionic dye MO and cationic dye MB. In detail, the GM adsorption property for the cationic dye is enhanced, while the adsorption property for the anionic dye is restrained. This phenomenon can be applied for separation of anionic and cationic dyes, which shows a new approach for waste-sorting treatment. According to isothermal adsorption study, the adsorption process follows the Langmuir isothermal adsorption, which indicates that the MB molecules are adsorbed homogeneously and distributed in the monolayer. The adsorption kinetics of the GM fits the pseudo-second-order model suggesting the adsorption process controlled by a chemical action. According to the diffusion mechanism research, the intraparticle diffusion is not the only rate-controlling step, and some other mechanisms such as boundary-layer adsorption are involved. In summary, this study provides a new solution for mass production of graphene functional materials at large scales with well-controlled

![Figure 10. Recyclability analyses of 5 mg of the GM in a 20 mL MB solution of 200 mg L\(^{-1}\).](image)
microstructures and surface properties, which showed superior performance in applications such as environmental remediation and selective separations.

4. MATERIALS AND METHOD

4.1. Apparatus and Materials. Natural graphite flakes with a size of 300 mesh (0.05 mm) are used as a precursor to produce graphene. The chemicals (37.5% HCl, 98% H2SO4, 30% H2O2, NaNO3, CaCl2, KMnO4, and ethanol) were purchased from Shanghai Titan Scientific Co., Ltd. l-Ascorbic acid, methylene blue, and methyl orange were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Sodium alginate was purchased from Aladdin Industrial Corporation. The nozzle was fabricated through a 3D printer provided by B9Creator (model B9C-BLACK V1.2). The syringe pump and the constant pressure pump used in the experiments are from Longer Precision Pump Co., Ltd. (model LSP02-1B) and Suzhou Wenhao Microfluidic Technology Co., Ltd. (Model WH-PMPP15), respectively. The air compressor is from ASL (model MOD 0930.2.2).

4.2. Preparation of Porous Graphene Microspheres. Graphene oxides are synthesized from natural graphite powder through a modified Hummer’s method.59 The graphene oxide ink is prepared as follows. First, 0.5 g of sodium alginate (SA) is dissolved into a 50 mL graphene oxide solution of 6 mg mL⁻¹, and then the mixed solution is kept in a water bath at 323 K for 1 h. In this procedure, the sodium alginate is used as the template of the porous framework. The nozzle used to produce microspheres is manufactured by a 3D printer using B9R-2-Black resin. The design of the nozzle is kept the same as in our previous work.38 Figure 1b shows the synthesis procedure where the as-prepared graphene oxide ink is sheared by the air flow via an inkjet nozzle to form microspheres. The gas-phase pressure is set to 0.015 MPa, corresponding to a flow rate of 50 mL min⁻¹, and then the microspheres are solidified in 10% CaCl2 solution for 12 h where the sodium alginate cross-links with Ca²⁺ to form calcium alginate gel and the calcium alginate gel becomes the framework of graphene microspheres, as shown in Figure 1b. The obtained microspheres are then rinsed under deionized water (DI water). The graphene oxide microspheres are reduced in l-ascorbic acid through the hydrothermal method to generate graphene microspheres (GMs). In detail, 10 mL of graphene oxide microspheres, 0.5 g of l-ascorbic acid, and 50 mL of DI water are added into a Teflon autoclave then the mixture is reacted in an oven under 453 K for 24 h. The GMs are rinsed by ethanol and DI water three times then dried in a freeze dryer for further use. For comparison, graphene oxide microspheres that have not been cured by sodium alginate are also prepared and reduced by the hydrothermal method to produce graphene bulk (GB). A 60 mL (6 mg mL⁻¹) graphene oxide solution with 0.5 g of l-ascorbic acid is added into the Teflon autoclave and reacted in an oven under 453 K for 24 h. The products are rinsed with ethanol and DI water and then dried in a freeze dryer. The unreduced graphene oxide microspheres are named GO.

4.3. Characterization of Materials. The formation process of droplets is recorded by high-speed camera Motion Xtra N4 (Integrated Device Technology), and the frequency is 200 Hz. The microstructures and morphologies of the GM and GB are characterized by a scanning electron microscope (SEM, Hitachi S-3400 N). X-ray diffraction (XRD) patterns of the GM, GB, and GO are acquired by a rotating anode X-ray powder diffractometer (Ragaku, 18KW/D/ max2550VB/PC) with monochromatic Cu Kα radiation, and the data of 2θ is scanned from 5° to 75° at a scan rate of 0.02° min⁻¹. Raman spectroscopy is done on the laser micro-Raman spectrometer (Renishaw inVia reflex) at the range of 500–2500 cm⁻¹ under the excitation wavelength of 514 nm and used for supplementary structure information analysis together with XRD. The thermogravimetric analysis (TGA) is carried out on a PerkinElmer Pyris 1 thermogravimetric analyzer, and the samples are heated from room temperature to 800 °C at a rate of 10 °C min⁻¹. Nitrogen adsorption/desorption isotherms at 77 K are performed on 3H-2000PS4 from BeishiDe Instrument Technology (Beijing) Co., Ltd. The specific surface area is calculated via the Brunauer–Emmett–Teller (BET) model, and the pore size distribution is attained via the Barrett–Joyner–Halenda (BJH) model. The Fourier transform infrared (FTIR) spectra are collected in the range of 500–4000 cm⁻¹ on a Nicolet 6700 Fourier transform infrared spectrometer.

4.4. Batch Adsorption Experiment. To investigate the selective adsorption performance of GMs and GB, cationic methylene blue (MB) and anionic methyl orange (MO) are chosen as the target organic pollutants. The effect of the initial concentration of methylene blue (MB) and equilibrium adsorption isotherms is determined in a batch adsorption experiment. The initial MB concentrations vary from 20 to 500 mg L⁻¹. The 5 mg adsorbent is added into a 20 mL MB solution, which is kept stirred for 12 h at 298 K. Then, the solution is filtered by nylon filter membranes to remove the adsorbent. The concentration of residual MB is detected via its absorbance at 664 nm on a UV–vis spectrophotometer (TU-1901, Beijing Purkinje General Instrument Co., Ltd). Finally, the adsorption capacity is calculated through eq 8.

\[ Q_e = \frac{(C_0 - C_e) V}{m} \]  

(8)

where \( Q_e \) (mg g⁻¹) is the adsorption capacity at equilibrium, \( C_0 \) (mg L⁻¹) is the initial MB concentration, \( C_e \) is the residual MB concentration at equilibrium, \( V \) (L) is the volume of the initial MB solution, and \( m \) (g) is the weight of the adsorbent. In comparison, the adsorption experiments for MO are carried out through the same procedures. The concentration of residual MO is determined via its UV–vis absorbance at 464 nm.

Moreover, the adsorption kinetics is investigated by varying the adsorption time. In detail, 5 mg of the adsorbent is added into a 20 mL MB solution of 100 mg L⁻¹. The concentration of MB is measured at different time intervals. The adsorption capacity is calculated through eq 9.

\[ Q_t = \frac{(C_0 - C_t) V}{m} \]  

(9)

where \( Q_t \) (mg g⁻¹) denotes the adsorption capacity at a certain time, \( C_0 \) (mg L⁻¹) is the initial MB concentration, \( C_t \) refers to the residual MB concentration at a certain time, \( V \) (L) stands for the volume of the initial MB solution, and \( m \) (g) is the weight of the adsorbent.

Experiments on selective adsorption of ionic and anionic pollutants are carried out to study the separation performance. Five milligrams of the adsorbent is mixed with 20 mL of MB and MO of 50 mg L⁻¹, respectively. The solutions are kept stirred for 12 h at 298 K. The residual concentrations of MO and MB are measured in the spectrum scanning mode of the UV–vis spectrophotometer in the range of 350–750 nm.
To investigate the recyclability performance of GMs, the used GM was eluted with methanol and 0.5 M CaC12 and washed subsequently with DI water. Then, the sample was lyophilized to remove the water.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02249.

Graphene droplet formation from the 3D-printed nozzle (MOV)

**AUTHOR INFORMATION**

Corresponding Authors
*E-mail: hxu@ecust.edu.cn (H.X.).
*E-mail: j.xuan@lboro.ac.uk (J.X.).

ORCID

Jin Xuan: 0000-0002-6718-9018

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The research presented in this paper is supported by the National Natural Science Foundation of China (no. 51776074), the Fundamental Research Funds for Central Universities (nos. 50321071917012 and 5032107198005), and the Royal Society in the U.K. via grant no. RSG \R1\180162.

**REFERENCES**

(1) Duru, I.; Ege, D.; Kamali, A. R. Graphene oxides for removal of heavy and precious metals from wastewater. J. Mater. Sci. 2016, 51, 6097–6116.

(2) He, K.; Chen, G.; Zeng, G.; Chen, A.; Huang, Z.; Shi, J.; Huang, T.; Peng, M.; Hu, L. Three-dimensional graphene support catalysts for organic dyes degradation. Appl. Catal., B, 2018, 228, 19–28.

(3) Li, X.; Yu, J.; Wągę, S.; Al-Ghamdi, A. A.; Xie, J. Graphene in Photocatalysis: A Review. Small. 2016, 12, 6640–6696.

(4) Ersan, G.; Apul, O. G.; Perreaud, F.; Karanfil, T. Adsorption of organic contaminants by graphene nanosheets: A review. Water Res. 2017, 126, 385–398.

(5) Chen, L.; Han, Q.; Li, W.; Zhou, Z.; Fang, Z.; Xu, Z.; Wang, Z.; Qian, X. Three-dimensional graphene-based adsorbents in sewage disposal: a review. Environ. Sci. Pollut. Res. 2018, 25, 25840–25861.

(6) Rethinasabapathy, M.; Kang, S.-M.; Jang, S.-C.; Huh, Y. S. Three-dimensional porous graphene materials for environmental applications. Carbon Lett. 2017, 22, 1–13.

(7) Huang, X.; Qi, X.; Boey, F.; Zhang, H. Graphene-based composites. Chem. Soc. Rev. 2012, 41, 666–686.

(8) Liu, T.; Li, Y.; Du, Q.; Sun, J.; Jiao, Y.; Yang, G.; Wang, Z.; Xia, Y.; Zhang, W.; Wang, K.; Zhu, H.; Wu, D. Adsorption of methylene blue from aqueous solution by graphene. Colloids and Surf., B 2012, 90, 197–203.

(9) Xiang, Q.; Yu, J.; Jaroniec, M. Graphene Based Semiconductor Photocatalysts. Chem. Soc. Rev. 2012, 41, 782–796.

(10) Zhao, F.; Dong, B.; Gao, R.; Su, G.; Liu, W.; Shi, L.; Xia, C.; Cao, L. A Three-dimensional Graphene-TiO2 Nanotube Nano-composite with Exceptional Photocatalytic activity for dye degradation. Appl. Surf. Sci. 2015, 351, 303–308.

(11) Shampa, P.; Sakia, B. K.; Das, M. R. Removal of methyl green dye molecule from aqueous system using reduced graphene oxide as an efficient adsorbent: Kinetics, isotherm and thermodynamic parameters. Colloids Surf., A 2014, 457, 125–133.

(12) Ramesha, G. K.; Vijaya Kumara, A.; Muralidhara, H. B.; Sampath, S. Graphene and graphene oxide as effective adsorbents toward anionic and cationic dyes. J. Colloid Interface Sci. 2011, 361, 270–277.

(13) Mi, X.; Huang, G.; Xie, W.; Wang, W.; Liu, Y.; Gao, J. Preparation of graphene oxide aerogel and its adsorption for Cu2+ ions. Carbon 2012, 50, 4866–4864.

(14) Riaz, M. A.; McKay, G.; Saleem, J. 3D graphene-based nanostructured materials as sorbents for cleaning oil spills and for the removal of dyes and miscellaneous pollutants present in water. Environ. Sci. Pollut. Res. 2017, 24, 27731–27745.

(15) Tiwari, J. N.; Mahesh, K.; Le, N. H.; Kemp, K. C.; Timilsina, R.; Tiwari, R. N.; Kim, K. S. Reduced graphene oxide-based hydrogels for the efficient capture of dye pollutants from aqueous solutions. Carbon 2013, 56, 173–182.

(16) Yu, P.; Wang, H.-Q.; Bao, R.-Y.; Liu, Z.; Yang, W.; Xie, B.-H.; Yang, M.-B. Self-Assembled Sponge-like Chitosan/Reduced Graphene Oxide/Montmorillonite Composite Hydrogels without Cross-Linking of Chitosan for Effective Cr(VI) Sorption. ACS Sustainable Chem. Eng. 2017, 5, 1557–1566.

(17) Bi, H.; Wan, S.; Cao, X.; Wu, X.; Zhou, Y.; Yin, K.; Su, S.; Ma, Q.; Sindoro, M.; Zhu, J.; Zhang, Z.; Zhang, H.; Sun, L. A General and Facile Method for Preparation of Large-scale Reduced Graphene Oxide Films with Controlled Structures. Carbon 2019, 143, 162–171.

(18) Cao, H.; Bi, H.; Xie, X.; Su, S.; Sun, L. Functional Tissues Based on Graphene Oxide: Facile Preparation and Dye Adsorption Properties. Acta Phys. Sin. 2016, 65, 148602.

(19) Ye, S.; Feng, J. Self-Assembled Three-Dimensional Hierarchical Graphene/Polyprrolyte Nanotube Hybrid Aerogel and Its Application for Supercapacitors. ACS Appl. Mater. Interfaces 2014, 6, 9671–9679.

(20) Ai, L.; Jiang, J. Removal of methylene blue from aqueous solution with self-assembled cylindrical graphene–carbon nanotube hybrid. Chem. Eng. J. 2012, 192, 156–163.

(21) Worsley, M. A.; Pauzauskie, P. J.; Olson, T. Y.; Biener, J.; Satcher, J. H., Jr.; Baumann, T. F. Synthesis of Graphene Aerogel with High Electrical Conductivity. J. Am. Chem. Soc. 2010, 132, 14067–14069.

(22) Zhao, X.; Yao, W.; Gao, W.; Chen, H.; Gao, C. Wet-Spun Superelastic Graphene Aerogel Millipores with Group Effect. Adv. Mater. 2017, 1701482.

(23) Zang, L.; Cao, X.; Zhang, Y.; Sun, L.; Qin, C.; Wang, C. Microfluidic generation of graphene beads for supercapacitor electrode materials. J. Mater. Chem. A 2015, 3, 22088–22093.

(24) Wang, J.; Jiang, J.; Cheng, Y.; Ding, H.; Zhao, Y.; Gu, Z. Microfluidic Generation of Porous Particles Encapsulating Spongy Graphene for Oil Absorption. Small 2015, 11, 3890–3895.

(25) Ma, T.; Chang, P. R.; Zheng, P.; Zhao, F.; Ma, X. Fabrication of ultra-light graphene-based gels and their adsorption of methylene blue. Chem. Eng. J. 2014, 240, 595–600.

(26) Hong, J.-Y.; Sohn, E.-H.; Park, S.; Park, H. S. Highly-efficient and recyclable oil absorbing performance of functionalized graphene aerogel. Chem. Eng. J. 2015, 269, 229–235.

(27) Lim, M. B.; Hu, M.; Manandhar, S.; Sakshaug, A.; Strong, A.; Riley, L.; Pauzauskie, P. J. Ultrafast sol-gel synthesis of graphene aerogel materials. Carbon 2015, 95, 616–624.

(28) Wang, C.-C.; Chen, H.-C.; Lu, S.-Y. Manganese Oxide/Graphene Aerogel Composites as an Outstanding Supercapacitor Electrode Material. Chem.-Eur. J. 2014, 20, 517–523.

(29) Liao, S.; Zhai, T.; Xia, H. Highly adsorptive graphene aerogel microspheres with center-diverging microchannel structures. J. Mater. Chem. A 2016, 4, 1068–1077.

(30) Zhu, C.; Han, T. Y.-J.; Duoss, E. B.; Gobolic, A. M.; Kuntz, J. D.; Spadaccini, C. M.; Worsley, M. A. Highly compressible 3D periodic graphene aerogel microlattices. Nat. Commun. 2015, 6, 6962.

(31) Wang, R.; Gao, W.; Li, X.; Liu, Z.; Liu, H.; Ding, S. Microfluidic generation of 3D graphene microspheres for high-efficiency adsorption. J. Mater. Sci. 2017, 52, 13930–13939.

(32) Hökke, A.; Henderson, H. T. Ultra-deep anisotropic etching of (110) silicon. J. Microchem. Microeng. 1999, 9, 51–57.

(33) He, B.; Tait, N.; Regnier, F. Fabrication of Nanocolumns for Liquid Chromatography. Anal. Chem. 1998, 70, 3790–3797.
(34) Unger, M. A.; Chou, H.-P.; Thorsen, T.; Scherer, A.; Quake, S. R. Monolithic Microfabricated Valves and Pumps by Multilayer Soft Lithography. Science 2000, 288, 113–116.

(35) Jiao, C.; Xiong, J.; Tao, J.; Xu, S.; Zhang, D.; Lin, H.; Chen, Y. Sodium alginate/graphene oxide aerogel with enhanced strength—toughness and its heavy metal adsorption study. Int. J. Biol. Macromol. 2016, 83, 133–141.

(36) Liu, R. C.; Lee, L. Y.; Hiew, B. Y. Z.; Thangalazhy-Gopakumar, S.; Gan, S. Environmental application of three-dimensional graphene materials as adsorbents for dyes and heavy metals: Review on ice-templating method and adsorption mechanisms. J. Environ. Sci. 2019, 79, 174–199.

(37) Ye, B.; Xu, H.; Bao, B.; Xuan, J.; Zhang, L. 3D-printed air-blust microfluidic nozzles for preparing calcium alginate microparticles. RSC Adv. 2017, 7, 48826–48834.

(38) Yang, S.; Zhang, L.; Yang, Q.; Zhang, Z.; Chen, B.; Lv, P.; Zhu, W.; Wang, G. Graphene aerogel prepared by thermal evaporation of graphene oxide suspension containing sodium bicarbonate. J. Mater. Chem. A 2015, 3, 7950–7958.

(39) Xu, X.; Li, H.; Zhang, Q.; Hu, H.; Zhao, Z.; Li, J.; Li, J.; Qiao, Y.; Gogotsi, Y. Self-Sensing, Ultralight, and Conductive 3D Graphene/Iron Oxide Aerogel Elastomer Deformable in a Magnetic Field. ACS Nano 2015, 9, 3969–3977.

(40) Jiang, G.; Lin, Z.; Chen, C.; Zhu, L.; Chang, Q.; Wang, N.; Wei, W.; Tang, H. TiO$_2$ nanoparticles assembled on graphene oxide nanosheets with high photocatalytic activity for removal of pollutants. Carbon 2011, 49, 2693–2701.

(41) Fei, Y.; Li, Y.; Han, S.; Ma, J. Adsorptive removal of ciprofloxacin by sodium alginate/graphene oxide composite beads from aqueous solution. J. Colloid Interface Sci. 2016, 484, 196–204.

(42) Liu, S.; Sun, H.; Liu, S.; Wang, S. Graphene facilitated visible light photodegradation of methylene blue over titanium dioxide photocatalysts. Chem. Eng. J. 2013, 214, 298–303.

(43) Cheong, M.; Zhitomirsky, I. Electrodeposition of alginic acid and composite films. Colloids Surf. A 2008, 328, 73–78.

(44) Xie, L.; Su, F.; Xue, L.; Li, X.; Liu, Z.; Kong, Q.; Guo, X.; Zhang, Y.; Lan, L.; Li, K.; Lv, C.; Chen, C. Self-Assembled 3D Graphene-Based Aerogel with Co$_3$O$_4$ Nanoparticles as High-Performance Asymmetric Supercapacitor Electrode. ChemSusChem 2015, 8, 2917–2926.

(45) Fan, J.; Shi, Z.; Lian, M.; Li, H.; Yin, J. Mechanically strong graphene oxide/sodium alginate/polyacrylamide nanocomposite hydrogel with improved dye adsorption capacity. J. Mater. Chem. A 2015, 3, 7433–7443.

(46) Wang, C.; Ding, Y.; Yuan, Y.; He, X.; Wu, S.; Hu, S.; Zou, M.; Zhao, W.; Yang, L.; Cao, A.; Li, Y. Graphene aerogel composites derived from recycled cigarette filters for electromagnetic wave absorption. J. Mater. Chem. C 2015, 3, 11893–11901.

(47) Chen, B.; Bi, H.; Ma, Q.; Tan, C.; Cheng, H.; Chen, Y.; He, X.; Sun, L.; Lim, T.-T.; Huang, L.; Zhang, H. Preparation of Graphene-MoS$_2$ Hybrid Aerogels as Multifunctional Sorbents for Water Remediation. Sci. China Mater. 2017, 60, 1102–1108.

(48) Yan, H.; Tao, X.; Yang, Z.; Li, K.; Yang, H.; Li, A.; Cheng, R. Effects of the oxidation degree of graphene oxide on the adsorption of methylene blue. J. Hazard. Mater. 2014, 268, 191–198.

(49) Yu, B.; Zhang, X.; Xie, J.; Wu, R.; Liu, X.; Li, H.; Chen, F.; Yang, H.; Ming, Z.; Yang, S.-T. Magnetic graphene sponge for the removal of methylene blue. Appl. Surf. Sci. 2015, 351, 765–771.

(50) Chen, L.; Yang, J.; Zeng, X.; Zhang, L.; Yuan, W. Adsorption of methylene blue in water by reduced graphene oxide: Effect of functional groups. Mater. Express 2013, 3, 281–290.

(51) Yu, R.; Shi, Y.; Yang, D.; Liu, Y.; Qu, J.; Yu, Z.-Z. Graphene Oxide/Chitosan Aerogel Microspheres with Honeycomb-Cobweb and Radially Oriented Microchannel Structures for Broad-Spectrum and Rapid Adsorption of Water Contaminants. ACS Appl. Mater. Interfaces 2017, 9, 21809–21819.

(52) Haque, E.; Jun, J. W.; Jiung, S. H. Adsorptive removal of methyl orange and methylene blue from aqueous solution with a metal-organic framework material, iron terephthalate (MOF-235). J. Hazard. Mater. 2011, 185, 507–511.

(53) Yao, Y.; Ying, H.; Feifei, X.; Xiaofeng, C. Equilibrium and kinetic studies of methyl orange adsorption on multwall carbon nanotubes. Chem. Eng. J. 2011, 170, 82–89.

(54) Zhao, S.; Chen, D.; Wei, F.; Chen, N.; Liang, Z.; Luo, Y. Synthesis of graphene oxide/metal–organic frameworks hybrid materials for enhanced removal of Methylene blue in acidic and alkaline solutions. J. Chem. Technol. Biotechnol. 2018, 93, 698–709.

(55) Rathinam, K.; Singh, S. P.; Li, Y.; Kasher, R.; Tour, J. M.; Arnusch, C. J. Polymide derived laser-induced graphene as adsorbent for cationic and anionic dyes. Carbon 2017, 124, 515–524.

(56) Cheng, Z.; Liao, J.; He, B.; Zhang, F.; Zhang, F.; Huang, X.; Zhou, L. One-Step Fabrication of Graphene Oxide Enhanced Magnetic Composite Gel for Highly Efficient Dye Adsorption and Catalysis. ACS Sustainable Chem. Eng. 2015, 3, 1677–1685.

(57) Jalil, A. A.; Triwahyono, S.; Adam, S. H.; Rahim, N. D.; Aziz, M. A. A.; Hairom, N. H. H.; Razali, N. A. M.; Abidin, M. A. Z.; Mohamadiah, M. K. A. Adsorption of methyl orange from aqueous solution onto calcined Lapindo volcanic mud. J. Hazard. Mater. 2010, 181, 755–762.

(58) Wang, P.; Cao, M.; Wang, C.; Ao, Y.; Hou, J.; Qian, J. Kinetics and thermodynamics of adsorption of methylene blue by a magnetic graphene-carbon nanotube composite. Appl. Surf. Sci. 2014, 290, 116–124.

(59) Hummers, W. S., Jr.; Offeman, R. E. Preparation of Graphitic Oxide. J. Am. Chem. Soc. 1958, 80, 1339–1339.