



## Full Length Article

## Preparation of novel oxidized mesoporous carbon with excellent adsorption performance for removal of malachite green and lead ion



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## ABSTRACT

An oxidized mesoporous carbon (OMC) with fluffy structure was fabricated from the mixture of petroleum asphalt and aluminum isopropoxide, and its structures were characterized by FESEM, TEM, BET, TG, XPS and FT-IR. In addition, bath adsorption experiments for malachite green (MG) and lead ion ( $\text{Pb}^{2+}$ ) were carried out to explore the effects of pH, initial concentration, contact time and temperature on its absorption process. Results show that the OMC prepared has a fluffy ultrathin-wall structure with narrow pore size distribution and rich oxygen-containing groups. It exhibits excellent absorption performance for the removal of MG as well as  $\text{Pb}^{2+}$ , as indicated by that its maximum adsorption capacity is  $963.1 \text{ mg g}^{-1}$  for MG and  $198.6 \text{ mg g}^{-1}$  for  $\text{Pb}^{2+}$ . The absorption experimental data are all fitted well with pseudo-second-order model and Freundlich isotherm, respectively. More importantly, the OMC still maintains relatively high adsorption capacity after five cycles.

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## 1. Introduction

Water pollution from organic dyes and heavy metals has directly threatened human health and ecological balance, which attracts great attention of international society. Organic dyes have board applications in food, paper, ink, and silk industries due to their low cost and ready availability. However, dye contaminated from these industries is becoming a principal environmental issue for their high toxicity, poor degradability and high solubility in water [1,2]. Malachite green (MG), as a basic synthetic dye, is commonly used as a food additives, parasiticide and antibacterial agent [3,4]. It is not only easy to enter the human body to cause carcinogenesis, mutagenesis, teratogenesis, respiratory diseases, and cancer, but also is extremely harmful to aquatic organisms and ecological environment [5,6]. In addition, lead (Pb) is one of toxic heavy metals which have widely application in batteries, fuels, metal plating, radiation protection material [7,8]. Lead pollution has harmful effects on environmental and human health because of its toxicity and non-biodegradable. The accumulation of lead in human body can cause anaemia, liver damage and encephalopathy [9–11]. Thus it is important to remove these contaminants before discharging into environment. At present, several methods have been reported to remove contaminants from water mainly including physical, chemical and biological methods [12–16].

Nevertheless, chemical and biological approaches are costly, complicated, or time-consuming, making them ineffective to completely remove the contaminants like MG and  $\text{Pb}^{2+}$  in large scale. Physical treatments including ion exchange, membrane filtration, precipitation, ozonation and adsorption are proved to be feasible methods to remove pollution from wastewater, among which adsorption is known to be a facile, low cost and high-efficiency method widely used to treat dyes and heavy metals.

In recent investigations, the most commonly used adsorbents are carbon materials such as activated carbon [17,18], mesoporous carbon [19,20] and graphene oxide (GO) [21–23]. In general, activated carbon is a widely used adsorbent because of its high surface area and porous structure. However, activation treatment usually generates micropores on its carbon surface, which generally results in a relatively low absorption capacity due to the size exclusion effect [24]. GO, which has a hexagonal network with oxygen-containing functional groups, can act as absorption sites for heavy metals or dyes, and therefore is considered as a suitable adsorbent in water purification. Mesoporous carbon has attracted increasing attention for the removal of pollutants from aqueous medium [24–30], due to its high specific surface area, well-developed pore structure, narrow pore size distribution, large pore volume and excellent thermal stability. Unfortunately, GO usually possesses lower accessible specific surface area and porosity due to the  $\pi$ - $\pi$  stacking of graphene sheets, while mesoporous carbon is insoluble and hard to disperse in solvents due to strong van der Waals interactions, which would bring adverse effects on adsorp-

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tion. So their adsorption performance has not been satisfactory, which is usually less than  $500 \text{ mg g}^{-1}$  for MG or  $200 \text{ mg g}^{-1}$  for  $\text{Pb}^{2+}$ . In addition, the applications of GO and mesoporous carbon for wastewater treatments are limited by some problems like poor absorption selectivity, small-scale preparation or high cost. Based on the above discussion, it is meaningful to fabricate a cost-effective mesoporous carbon material, which inherits both the advantages of mesoporous carbon and GO for achieving excellent adsorption performance with improved absorption selectivity.

To date, oxidized carbonaceous materials with oxygen-containing functional groups can be prepared by many methods (e.g., dry oxidation and wet oxidation), and which has been widely used as adsorbents. However, the oxidization of conventional mesoporous carbon usually stays on its surface due to both dense structure and relatively small pore diameter, and therefore the oxidized mesoporous carbon (OMC) is also difficult to use as a high-performance adsorption material. As a solution, we introduce a graphitic mesoporous carbon (GMC) to prepare OMC with desired adsorption performance. As is well known, graphitic carbon material can be easily oxidized to obtain GO-like structure by Hummers method, which possesses rich oxygen-containing functional groups with improved solubility and dispersity. In our previous work [31], a fluffy GMC with ultrathin walls had been successfully prepared by direct carbonization of the mixture of petroleum asphalt and aluminum isopropoxide. It is generally accepted that ultrathin graphitic structure has strong interactions with planar molecules like organic dyes or heavy metals [32–34]. In addition, the GMC had a fluffy structure with a large average pore size (7.54 nm) and a relatively high pore volume ( $1.55 \text{ cm}^3/\text{g}$ ) [31], which seems to be suitable for achieving the GO-like structure by deep oxidation via Hummers method. To our knowledge, there are relatively few investigations on using modified Hummers method to obtain oxidized graphitic carbon adsorbent. What's more, the existed traditional adsorbents (e.g., mesoporous carbon, chitosan, etc.) are generally available for the adsorption of one pollutant or a type of pollutant, and there are less efficient adsorbents which can remove the mixed contaminants (e.g., dyes and heavy metals) [14]. Therefore, it is meaningful to develop an efficient adsorbent for the treatment of heavy metals and dyes simultaneously. In this work, a novel oxidized mesoporous carbon (OMC) was fabricated from the GMC followed by oxidation via a modified Hummers method, and its removal capacity of MG and  $\text{Pb}^{2+}$  was investigated.

## 2. Experiment

### 2.1. Raw material

Petroleum asphalt was supplied by China Offshore Bitumen Co, Ltd, and its main properties were shown as follows: softening point,  $40^\circ\text{C}$ ; asphaltene, 39.4 wt%; resins, 28.2 wt%; aromatics, 16.1 wt%; saturates, 10.9 wt%. Aluminum isopropoxide (purity, >99.9%), potassium permanganate powder ( $\text{KMnO}_4$ , >99.5%), sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%), hydrochloric acid (HCl, 36–38%), sodium nitrate ( $\text{NaNO}_3$ , >99%), hydrogen peroxide aqueous solution ( $\text{H}_2\text{O}_2$ , 30 wt%), malachite green (MG) and lead (II) nitrate ( $\text{PbNO}_3$ , >99%) were obtained from Sinopharm Chemical Reagent Co. Ltd. All chemicals were analytical grade without any purification in the experiments.  $0.1 \text{ mol L}^{-1}$  HCl and  $0.1 \text{ mol L}^{-1}$  NaOH were used for pH adjustment and instantly prepared when needed.

### 2.2. Preparation of the OMC

The GMC was firstly prepared by direct carbonization of the mixture of petroleum asphalt and aluminum isopropoxide described in our previous work [31]. The OMC was prepared via

a modified Hummers method described as follows:  $\text{H}_2\text{SO}_4$  (20 mL) was added into the mixture of GMC (1.0 g) and  $\text{NaNO}_3$  (0.5 g), and  $\text{KMnO}_4$  (3.0 g) was slowly added with continuously stirring in an ice-water bath for 2 h, and then placed in the  $35^\circ\text{C}$  water bath for 2 h. Then, 250 mL of deionized water was added, followed by adding 10 mL of  $\text{H}_2\text{O}_2$  (30%). After that the resulting samples was filtered and washed with deionized water for several times until the filtrate became neutral, and finally freeze-dried for further use.

### 2.3. Characterization

The morphologies and element contents of samples were identified by field emission scanning electron microscopy (FESEM, Carl Zeiss ULTRA 55). The structure analysis was conducted by Transmission electron microscopy (TEM, JEM-2010, Jeol). Thermal gravimetric analysis (TGA) was performed on a thermogravimetric analyzer (TGA, SDT-Q600) under nitrogen atmosphere with the heating rate of  $10^\circ\text{C min}^{-1}$ .  $\text{N}_2$  adsorption–desorption isotherms of samples were performed at 77 K in a physical adsorption apparatus (3Flex, Micromeritics). The specific surface areas and pore size distributions curves of the materials were calculated using the Brunauer–Emmett–Teller (BET) method in a relative pressure range of 0.05–0.3 and density functional theory method, respectively. Fourier transformed infrared (FT-IR) spectra of the samples were studied on a FT-IR spectrophotometer (Nicolet 5700). Elemental analysis was studied using a X-ray photoelectron microscopy (XPS, PHI 5000 Versa Probe). The zeta potential of the OMC aqueous suspensions ( $1 \text{ g L}^{-1}$ ) was performed on a zeta potential analyzer (Nano-S Zetasizer, Malvern Instruments Ltd), and the pH of the sample was adjusted to 2–10 by adding HCl or NaOH. The concentrations of MG solution and  $\text{Pb}^{2+}$  solution after batch experiments were determined with UV–Visible spectrophotometer (Jasco model V-530, Japan) at 618 nm and atomic absorption spectrometry (AAS, SHIMADZA AA-6880), respectively.

### 2.4. Adsorption studies

In order to study the removal capacity of MG and  $\text{Pb}^{2+}$ , 0.01 g of the OMC was put into conical flask containing 20 mL aqueous solution with various initial concentrations ( $200\text{--}700 \text{ mg L}^{-1}$  for MG and  $25\text{--}200 \text{ mg L}^{-1}$  for  $\text{Pb}^{2+}$ ) at a constant temperature for 24 h. The pH of the solutions (from 2 to 8 for MG, and from 2 to 6 for  $\text{Pb}^{2+}$ ) was adjusted using diluted NaOH or HCl solution. The influence of temperature was performed by various temperatures ( $25\text{--}50^\circ\text{C}$ ). The samples were filtered at desired time intervals to explore the effect of contact time. All adsorption experiments were performed at least three times. The adsorption capacity  $Q_t$  ( $\text{mg g}^{-1}$ ) and removal percentages (R%) was calculated using the following equation:

$$Q_t = [(C_0 - C)V]/m \quad (1)$$

$$R\% = (C_0 - C)/C_0 \times 100\% \quad (2)$$

where  $m$  (g) is the mass of the OMC,  $V$  (L) is the volume of the MG solution,  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial concentration of the dye, and  $C_e$  is the equilibrium concentrations in solution.

### 2.5. Desorption studies

The OMC (0.01 g) was first loaded with  $\text{Pb}^{2+}$  or MG dyes at optimum conditions, respectively, and then the desorption of MG and  $\text{Pb}^{2+}$  from the OMC was performed in ethanol and diluted NaOH solutions for 12 h at room temperature, respectively [35,36]. The obtained products were washed with deionized water and dried

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