# Adsorption of malachite green from aqueous solutions onto ordered mesoporous carbons

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## ARTICLE INFO

## ABSTRACT

The carbon materials with well-ordered mesoporous tubular structure were synthesized, which were confirmed by transmission electronmicroscopy (TEM), Raman spectrum, small angle X-ray diffraction (XRD), and $N_2$ adsorption/desorption analysis. Moreover, by adjusting the ratio of furfuryl alcohol (FA) and trimethylbenzene (TMB), the structural parameters of the ordered mesoporous carbons (OMCs) could be facilely tuned. The materials synthesized were applied as a host in adsorption MG molecules. The carbon materials after the adsorption of Malachite green (MG) were also characterized by XRD and $N_2$ adsorption/desorption analysis. The results showed that the adsorption of MG had not greatly changed the basic ordered pore structure of the OMCs. The mixed 1,2-order equation(MOE) was suitable for the dynamic adsorption of MG on OMCs. Thermodynamic parameters of adsorption such as free energy change and enthalpy change were obtained from the equilibrium constants at different temperatures. The thermodynamic data indicated that MG adsorption onto OMCs was a spontaneous and exothermic physical process.

## 1. Introduction

It is no denying that Malachite green (MG), as a hazardous triphenylmethane compound as well as bactericide, has been commonly used as an antifungal agent in aquatic systems such as fish hatcheries for the persuit of large economic benefits. However, MG was prohibited due to the high toxicity, high residues and high carcinogenicity [1–4]. People have paid close attention to the unpredictable water pollution problems thus generated. There is no doubt that a high efficient adsorbent is in great demand for the treatment of MG in aquatic system to reduce the hazard to environment.

OMCs, due to their remarkable properties such as high specific surface area, narrow pore size distribution, tunable pore structure, large pore volume and high thermal and mechanical stability, have attracted great technological interest for the development of purification of water, electronic, catalytic and energy storage systems [5–10]. Moreover, the excellent biocompatibility and controllable pore size distributions make them highly prospective and valuable in water pollution control. Various studies have proved the validity of porous materials for the removal of organic and inorganic pollutants [11–21]. Therefore, it was interesting to study the adsorption

and treatment of MG onto OMCs both for fundamental research and applications, especially as to our knowledge, the adsorption and thermodynamic studies of MG onto OMCs has not been previously reported.

In the present contribution, OMCs with the controlled structural parameters were synthesized by using FA as carbon precursor and the adsorption of MG onto OMCs were carried out. The effects of structural parameters of the OMCs and temperature on adsorption were investigated. In addition, dynamic and thermodynamic studies were also carried out to investigate the adsorption mechanism of MG onto OMCs.

## 2. Experimental

### 2.1. Synthesis of OMCs

The synthesis of SBA-15-100 template referred to the previously reported literature [22,23]. The hydrothermal temperature was kept at 373 K and the resulting pyrolysized sample was labeled as SBA-15-100. For the synthesis of OMCs, the typical process similar to what A. Lu reported [24] was as follows. 1 g of SBA-15-100 (vacuum dried at 333 K for 8 h before use) was impregnated in 2.0 ml of Furfural Alcohol/Trimethylbenzene (FA/TMB) solution at different ratios ($v/v$, 1:1, 2:1, 3:1) by incipient wetness at room temperature. Then, 0.1 g of oxalic acid was added as a polymerization catalyst. The resulting composite was heated at 353 K for 12 h and then at

423 K for 6 h for the polymerization of FA. After cooling to room temperature, the samples were heated to 573 K (1 K/min), then to 1173 K (5 K/min) and kept the pyrolysis process for 4 h under flowing argon atmosphere (200 ml/min). The obtained black powder was washed with HF (20%), filtered and washed repeatedly with water and then with ethanol until the pH value was close to 7. Finally, the samples were dried at 313 K under vacuum for 24 h. The resultant carbon materials were referred to as C-1, C-2, and C-3, respectively.

All chemicals used in this study were analytical reagent (A.R.). The water used was deionized water.

### 2.2. Adsorption of malachite green (MG)

In the adsorption experiment, a typical process was as follows: different weight of carbon materials was added into 25 ml of MG solution with initial concentration of 20 mg/l. The resulting mixture was continuously stirred (rotation speed was 200 rpm) in a closed batch at pre-settled temperature until equilibrium was reached. This was done by monitoring the MG concentration using a UV–vis spectrophotometer at a wavelength of 617 nm. The amount of MG adsorbed onto the samples was determined according to the change of concentration before and after adsorption. In dynamic studies, typical experiments were done by adding 0.07 g of OMCs into 1000 ml of solution containing 20 mg/l of MG at different time intervals.

The adsorption amount of MG onto the OMCs ($q_e$) was calculated according to the following equation:

$$q = \frac{V(C_0 - C)}{W} \qquad (1)$$

where $C_0$ and $C$ were the initial and temporary concentrations of MG (mg/l); $V$ was the volume of the solution (l); and $W$ was the mass of OMCs (g).

### 2.3. Characterization

Characterizations such as powder X-ray diffraction, nitrogen sorption at 77 K, transmission electron microscopy (TEM) and Raman spectroscopy were taken. The small angle XRD patterns (XRD) were recorded on a Multi Purpose Diffractometer (PANanalytical. Inc. X'Pert Pro., MPD) with Cu Kα radiation (0.1540 nm), using an operating voltage of 40 kV and 40 mA. Microscope glass slides were used as sample supports. The samples were manually ground prior to the XRD analysis and all measurements were performed at room temperature. Nitrogen sorption isotherms were measured with Tristar 3020 volumetric adsorption analyzer (Micrometrics) at 77 K. Before adsorption, samples were degassed under vacuum at 473 K for 4 h. After adsorption of MG, samples were degassed at 313 K for 24 h. The specific surface area of the samples was calculated by using the BET method. The pore size distributions were derived from the adsorption branches of isotherms by using the Barett–Joyner–Halenda (BJH) model, and the total pore volumes ($V_t$) were estimated from the adsorbed amount at a relative pressure $p/p_0$ of 0.99. The mean hydraulic pore diameters were calculated from the BET specific surface area and the pore volume ($D = 4V_t/S_{BET}$)[25]. TEM experiments were taken on a JEOL 2011 microscope operated at 200 kV. The samples for TEM measurements were suspended in ethanol and supported onto a holey carbon film on a Cu grid. Raman spectroscopy measurements were made on a HORIBA Jobin Yvon LabRAM Aramics with a microscope attachment, using a He–Ne laser with a wavelength of 633 nm. The UV–visible absorption spectra values were measured on a U-3010 spectrophotometer (Hitachi).

## 3. Results and discussion

### 3.1. TEM images and Raman spectroscopy of as prepared OMCs

Fig. 1 showed the TEM images of C-1 perpendicular to the channel (A) and along the channel (B). The ordered arrangement of mesopores was clearly observed in the direction perpendicular to the channel, giving direct evidence for the presence of ordered mesoporous carbon (Fig. 1A). A hexagonally ordered array of circles could also be observed along the pore channels (Fig. 1B), which confirmed the CMK-5 structure [24,26,27]. It was worth noting that two types of pores could be clearly identified. The white points surrounded by dark lines were the projection of the tubular interiors, which corresponded to the pores generated in the inner part of the SBA-15 channels that were not filled with the carbon, where the white circles between the dark rings were images of the pores originated from the mesopores generated in the space previously
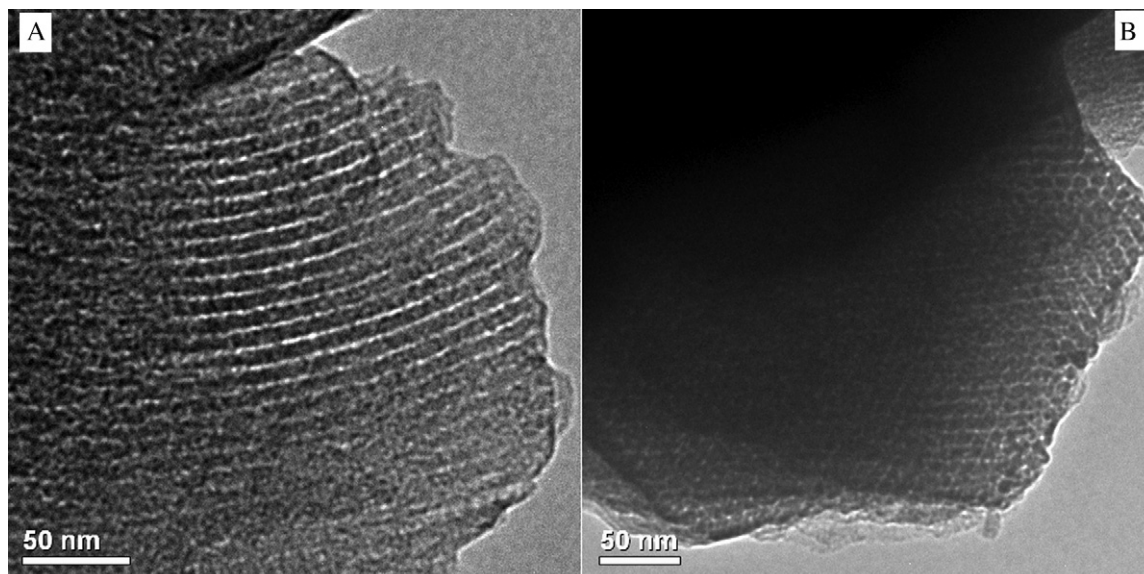


**Fig. 1.** The TEM images of C-1 viewed perpendicular to the channel (A) and along the channel (B).