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# Removal of anthracenemethanol from soil through a magnetic system assisted by ceramsite coated with nanoflower-structured carbon and preparation for its engineering application

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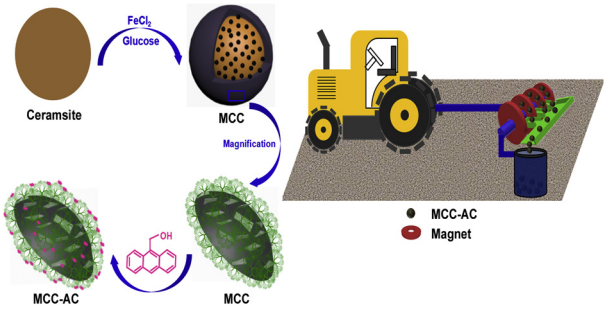
## HIGHLIGHTS

- A magnetic ceramsite system (OMCCNC) was facilely prepared by hydrothermal treatment.
- OMCCNC possessed a high removal efficiency for anthracenemethanol (AC) from soil.
- The OMCCNC-AC mixture after adsorption can be separated and collected conveniently.

## GRAPHICAL ABSTRACT

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## ABSTRACT

This work reported a facile approach to remove anthracenemethanol (AC), a typical polycyclic aromatic hydrocarbon (PAH), from soil using magnetic ceramsite coated with nanoflower-structured carbon (MCCNC), whose optimal form was named as OMCCNC, fabricated by a one-step hydrothermal process. Therein, the carbon coating self-assembled to form a flower-like fractal structure based on the template of micro-nano flakes on the surface of ceramsite. The nanoflower-structured carbon possessed a high porosity and plenty of oxygen-containing groups and thus could efficiently adsorb AC molecules. After adsorption, the high magnetism of OMCCNC facilitated the continuous separation and collection of OMCCNC-AC from soil using a magnetic separation system (MSS) designed by us. Importantly, the OMCCNC could be reused at least for four times. This work provides a promising approach for removing AC from soil and may have a huge engineering application prospect.



## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), composed of two or more fused aromatic benzene rings, are discharged into environment along with the development of anthropogenic activities, such as agricultural production, residential waste burning and the utilization of petroleum products [1]. The removal of PAHs from water and soil attracted more and more attention because their

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hydrophobic, chemical stable and anti-biodegradation properties intensified their toxic, carcinogenic, mutagenic effects to human beings [2–4]. Various treatment approaches have been widely developed to remove PAHs from contaminated water, including physical (incineration, solvent leaching and extraction) [5], chemical (oxidation and photocatalytic degradation) [6–9] and biological (phytoremediation and enzyme technology) processes [10,11]. However, most of these methods displayed several disadvantages such as formation of secondary pollutants, high cost, complicated procedure and time-consuming in different extents. Therefore, a facile and fast approach should be developed to meet the demand [12,13]. Recently, adsorption was found to be a promising method to remove PAHs from water using adsorbents including activated carbon, biochar, molecular sieve and graphene oxide and so on [12–15]. Some researches have been reported on the removal of PAHs from soil through adsorption using biochar, activated carbon, clays and humic acid. However, it was still a challenge to collect and reuse these materials from soil because of their micro-nano sizes [6]. Therefore, to remediate the PAHs-contaminated soil through adsorption, it is rather important to develop efficient used-in-soil adsorbents and separation approaches.

Ceramsite, derived from nano clay, mineral or waste sludge, has been widely used as carriers for adsorbents in water treatment due to the properties of high porosity, large pore diameter, sufficient mechanical strength and favorable biocompatibility [15,16]. However, until now ceramsite has been rarely used in soil, which is mainly because of the lack of adsorption ability and difficulty of separation. If a carbon layer is fabricated on the surface of ceramsite, it will have a high adsorption capacity. In addition, the ceramsite modified by $Fe_3O_4$ could display a magnetic property and thus be easily separated by external magnetic field, resulting in a good regeneration capacity.

This work describes an approach to fabricate a new adsorbent, magnetic ceramsite coated by nanoflower-structured carbon (MCCNC), which possessed a high magnetism and adsorption capacity on PAH in soil. The optimal condition of the fabrication process of MCCNC was investigated and the resulting product was designated as OMCCNC. As a kind of typical PAH, anthracenemethanol (AC) was selected as the target pollutant in this work [17]. Therein, the effects of AC initial concentration, pH and coexistent substances on the removal efficacy of OMCCNC were further investigated, and the mechanism of the removal process was also studied. Importantly, a magnetic separation system (MSS) was designed by us to continuously separate and collect the OMCCNC-AC mixture from soil, which can facilitate the regeneration of OMCCNC. This work provides a promising and facile systematic approach to remove organic contaminant from soil and may have a huge engineering application potential.

## 2. Experimental

### 2.1. Materials

Anthracenemethanol, $FeCl_2$, glucose, urea, KCl, NaCl, $MgCl_2$, $CaCl_2$, HCl, and NaOH with analytical grade and humic acid (HA) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Raw ceramsite (RC) (mainly composed of $SiO_2$, $Al_2O_3$, CaO, $MgCl_2$, $Na_2O$, and $K_2O$) with an average diameter of 5 mm were provided by Xuan Dong Co., Ltd. (Hangzhou, China). Deionized water was used throughout this work.

### 2.2. Preparation of MCCNC

MCCNC was synthesized as the following methods. Firstly, RCs were soaked in HCl solution (3 mol $L^{-1}$) at 25 °C for 12 h. Subsequently, the system was filtered by a 100 mesh sieve to collect the resulting ceramsite which were washed with 500 mL deionized water for three times and then dried at 60 °C for 12 h to obtain acid modified ceramsite (AMC). After that, $FeCl_2$ (1.0 g) was dissolved in 30 mL of deionized water containing 2.0 g of AMC under continuously stirring for 30 min (300 rpm), and then glucose with different weight ratio ($WFeCl_2/W_{glucose}$ = 3:1, 2:1, 1:1, 1:2 or 1:3) was added to the mixture under continuously stirring for 30 min (300 rpm). Then urea (2.0 g) was added to the resulting system to provide an alkaline condition which was beneficial for the fabrication of $Fe_3O_4$ [18]. The system was kept stirring for 30 min and then transferred into the polytetrafluoroethylene (PTFE)-lined stainless steel autoclave for hydrothermal treatment under different temperatures (140, 160, 180, and 200 °C) and reaction time (4, 6, 8, 12, 16, and 24 h) after stirring for 30 min. Finally, MCCNC was obtained after three washing-magnetic separation cycles and dried at 80 °C for 12 h. The resulting MCCNC fabricated with $WFeCl_2/W_{glucose}$ of 3:1, 2:1, 1:1, 1:2 and 1:3 are designated as MCCNC-3:1, MCCNC-2:1, MCCNC-1:1, MCCNC-1:2, and MCCNC-1:3, respectively.

### 2.3. Preparation of other samples

In order to make a comparison, some other samples based on ceramsite were also prepared. Hydrothermally treated AMC (HTAMC) was fabricated using the following method. Firstly, 2.0 g of AMC was added in 30 mL of deionized water under continuously stirring (300 rpm for 30 min), and then the whole mixture was transferred into the PTFE-lined stainless steel autoclave for hydrothermal treatment under 200 °C with reaction time of 24 h. Finally, HTAMC was obtained after three washing-centrifugation (10,000 rpm for 5 min) cycles and dried at 80 °C for 12 h.

To fabricate ceramsite@carbon (CC), glucose (2.0 g) and AMC (2.0 g) were added to 30 mL of deionized water under continuously stirring (300 rpm for 30 min), and then the resulting mixture was transferred into a PTFE-lined stainless steel autoclave for hydrothermal treatment under 200 °C for 24 h. Finally, CC was obtained after three washing-centrifugation (10,000 rpm for 5 min) cycles and dried at 80 °C for 12 h.

In addition, the $Fe_3O_4$ modified ceramsite ($Fe_3O_4$-AMC) could be obtained by the procedure similar to that of MCCNC. Firstly, $FeCl_2$ (1.0 g) was dissolved in 30 mL of deionized water containing 2.0 g of AMC under continuously stirring (300 rpm for 30 min). Secondly, urea (2.0 g) was added to the resulting system which was then hydrothermally treated at 200 °C for 24 h after stirring for 30 min. Finally, $Fe_3O_4$-AMC was obtained after three washing-magnetic separation cycles and then dried at 80 °C for 12 h.

### 2.4. Investigation of the removal efficiency of AC from water

The removal efficiencies of HTAMC, CC, $Fe_3O_4$-AMC and MCCNC on AC from water were investigated respectively. Each sample (3.0 g) was added to 50 mL of AC aqueous solution (10 mg $L^{-1}$) under continuously stirring (300 rpm) at 25 °C. 2 mL of the resulting suspension was centrifuged at 10,000 rpm for 5 min, and then the concentration of AC in the supernatant was measured [17]. The removal efficiency (RE) could be calculated using the following equation:

$$RE = (C_0 - C_t)/C_0 \times 100\% \quad (1)$$

where $C_0$ and $C_t$ were the initial and residual concentrations of AC, respectively.