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MPC-973: A low-cost and effective adsorbent for the removal of nitrobenzene from aqueous solutions

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HIGHLIGHTS

- A series of low-cost magnetic porous carbon (MPC) were prepared via one-step pyrolyzation method.
- MPC-973 presented the best NB adsorption capacity of 58.2 mg g^{-1} at 288 K.
- MPC can be separated from aqueous solution under an external magnetic field.
- The adsorption mechanism of NB on MPC is heterogeneous adsorption.

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ABSTRACT

A series of low-cost magnetic porous carbons (MPCs) were prepared via a pyrolyzation method using peanut shells as carbon resource and hydrochloric acid pickling wastewater as magnetic precursor. The physical-chemical properties were characterized by XRD, SEM, FTIR and BET technologies. The adsorption experiments of nitrobenzene (NB) on MPCs show that the adsorption performances were significantly affected by the carbonization temperature and MPC-973 presented the best adsorption capacity of 58.2 mg g^{-1} at 288 K, which can be kept up to 82.2% even after six cycles. The obtained MPC can be recycled from aqueous solution under an external magnetic field reveals there is a good magnetism. The kinetics and isotherm results demonstrate that the adsorption mechanism of NB on MPC is heterogeneous adsorption, including surface area, porous structures, H-bond interaction, the π-π interaction and electrostatic interaction between the adsorbent MPC and NB molecules.

1. Introduction

As an important raw industrial material, nitrobenzene has been widely used in the dyes, explosives and pesticides [1,2]. Nitrobenzene shows high risks to ecological and human health even at a low concentration, owing to its toxicity, poor biodegradability, and combustibility, which has been nominated by the National Institute of Environmental Health Sciences to present in the Report on Carcinogens [3]. Thus, many researchers devote themselves to the removal of NB from aqueous environment. So far, traditional methods for the removal of NB mainly include reduction, oxidation, filtration, coagulation, ion exchange, perception and adsorption, etc [4–7]. Adsorption method is generally regarded as a better choose due to its obvious advantages, such as simple operation, safety, low-cost and effectiveness.

In general, activated carbon with high surface area can be considered the most economical and efficient adsorbent to removal of NB from wastewater. However, the small particle size, high regeneration temperatures, and unsuitable hydrophilic/oleophilic properties sometimes seriously prevent its applications [8–10]. Recently, many magnetic carbon materials have been prepared using a two-step method, which offer an opportunity to realize magnetic auxiliary separation by an external magnet. In brief, the mesoporous carbon materials are first prepared, followed by the infiltration of magnetic nanoparticles into the mesopores or hollow cores [11–13]. Unfortunately, the two step method has some inevitable disadvantages, such as complexity, high-cost and the loss of adsorption capacity during recycle.

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Herein, magnetic porous carbon materials (MPCs) were synthesized via a simple one-step method using peanut shells as carbon resource and hydrochloric acid pickling wastewater as magnetic precursor, which combine the advantages of low-cost, high surface areas, hierarchical micropore structure, good magnetic separability, and suitable hydrophobic/oleophilic properties. NB was chosen as a representative to evaluate the adsorption ability of the obtained MPCs. In order to explore the adsorption mechanism of NB, the adsorption kinetics and isotherm models were furthermore investigated.

2. Experimental

2.1. Materials

Hydrochloric acid pickling wastewater was obtained from local stainless steel industry. Nitrobenzene was purchased from Tianjin Chemical Reagent Company, which is analytical grade, without further treatment before using.

2.2. Preparations of magnetic carbon materials

MPC were prepared according to the previous report [14]. In brief, 20 g local peanut shells were washed using deionized water (second degree) for several times, dried and cut into 4–8 mesh. Then, the obtained peanut shells was dispersed in 240 mL hydrochloric acid pickling wastewater (its composition can be found in Table 1 from reference [14]) with ultrasonic for 4 h to ensure the magnetic element $FeCl_3$ and $NiCl_2$ can be sufficiently adsorbed on the peanut shells. The impregnated sample was dried at 110 °C for 12 h and carbonized under N_2 atmosphere at 773 K, 973 K and 1073 K for 2 h in the step of 5 °C min^{-1}. The final product of magnetic porous carbon was named MPC-773, MPC-973 and MPC-1073 (where the "773" "973" and "1073" refers to the carbonization temperatures).

2.3. Characterization of MPC

The crystalline structures test of the obtained MPC was conducted on a D8 advance X-ray diffractometer (Bruker, USA) using Cu Kα radiation. The N_2-adsorption isotherms of the samples were performed by using a Micromeritics ASAP 2020 system (Micromeritics, USA). Scanning electron microscopy (SEM) analysis was conducted using a JSM-6490-LV electron microscope (JEO, Japan). Fourier transform infrared spectra were recorded on a NICOLET380 FTIR spectrophotometer (Thermo Nicolet Co., USA).

2.4. Adsorption performance of NB

The effect of carbonization temperature and the recycle test were performed by mixing 30 mg MPC samples with a 40 mL NB aqueous solution in 150 mL stirred flask at 298 K for 2 h. The adsorption isotherm and kinetics experiments of NB on MPC-973 were performed on the basis of a batch experiment. After the adsorption equipment achieved, the adsorbents MPC were separated using magnetic assisted separation technology. The equilibrium concentrations of NB were measured by a UV spectrometer (T6 Model, Beijing, China) at 268 nm. The equilibrium adsorption amount was calculated by using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where C_0 and Ce (mg L^{-1}) are the initial and equilibrium concentrations of NB, respectively. V is the volume of the NB aqueous solution (mL) and W is the weight of MPCs (g).

Table 1
Surface area and pore structure of the MPC obtained at different carbonization temperatures.

Samples	BET surface area (m^2 g^{-1})	Average Pore size (nm)
MPC-773	673	56.7
MPC-973	1034	12.5
MPC-1073	752	8.2

3. Results and discussion

3.1. Characterization of MPC

The crystalline structures of the carbon materials carbonized at different temperature were investigated by powder X-ray diffraction. XRD patterns of MPC-773, MPC-973 and MPC-1073 are shown in Fig. 1. The weak peaks at 26.2° in all patterns reveals the obtained carbon materials present in the graphite structure [15,16]. The results confirm that the peanut shells after carbonization in the presence of iron turn into carbon structures with some degree of graphitic order. The peaks at 16.1° and 20.8° at all XRD patterns can be assigned to lepidocrocite α-FeOOH [17]. In addition, the crystal structure of Fe_2O_3 and Fe_3O_4 also can be found. Their intensity increases with the increasing carbonized temperature. It indicated the aggregation of magnetic particles at high calcination temperature [18]. In addition, no peak of Ni species can be found in all samples, owing to its amount below the detection limit.

FTIR spectra were employed to identify the surface functional groups in MPC and to evaluate the bonding interaction between the obtained carbon materials and magnetic particles. The FTIR spectra of MPC-773, MPC-973 and MPC-1073 are shown in Fig. 2. The broad peaks at about 3400 cm^{-1} and the shoulder at 3186 cm^{-1} presented in all FTIR spectra. The peaks can be attributed to the stretching vibration of O-H, which indicates the presence of O-H groups on the surface of the prepared MPC [19,20]. The bands at around 2193 cm^{-1} and 1600 cm^{-1} correspond to C=O and C-O stretching vibrations, demonstrating the existence of carboxylic acids group [14,21]. While the weak band at 1086 cm^{-1} appears in the FTIR spectra of MPC-773 and MPC-973, which can be attributed to C-O stretching of lactonic, ether, phenol, etc [22]. By comparison, it can be found that the relative intensity of the oxygen-containing

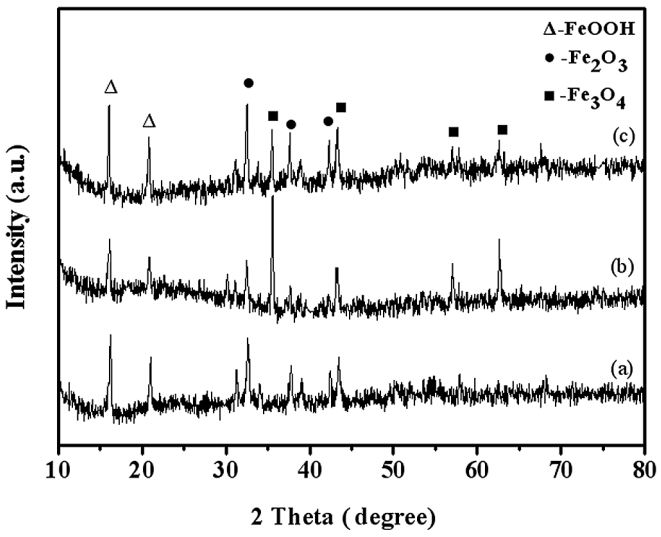

Fig. 1. XRD patterns for (a) MPC -773, (b) MPC -973 and (c) MPC-1073.