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An Acid-resistant Magnetic Co/C Nanocomposite for Adsorption and Separation of Organic Contaminants from Water

RUAN Chang-Ping[1,2], AI Ke-Long[1,]*, LU Le-Hui[1]

[1] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

[2] University of Chinese Academy of Sciences, Beijing 100049, China

Abstract: Magnetic adsorbents have recently been extensively investigated and applied in the field of water purification, because of their magnetic characters which are advantageous for the separation and recycle of these materials. Unfortunately, common magnetic materials are unstable and prone to dissolution in acid environment, thus limiting their practical applications in wide pH range, particularly in acidic condition. Therefore，it is highly imperative to exploit a novel magnetic adsorbent that is acid-resistant, to simplify separation process during the water purification. In present work, an acid-resistant magnetic Co/C nanocomposite was synthesized by using ZIF-67 as both template and precursor. The ZIF-67 was carbonized in an argon atmosphere at 800 ºC for 1 h, and then treated with acid. Upon calcination at an appropriate temperature in inert atmosphere, the generated Co nanoparticles were uniformly wrapped by graphite layers, due to the graphitization of carbon upon the catalysis effect of Co. The formed graphite layers were able to protect the Co particles from oxidation and acid environment, thus resulting in the generation of an acid-resistant magnetic adsorbent that can be applied in a wide pH range (pH 1–13). Remarkably, the as-synthesized magnetic Co/C nanocomposite demonstrated excellent adsorption performance towards two typical organic dyes (rhodamine B and malachite green) over a wide pH range. The adsorption isotherms of rhodamine B and malachite green on Co/C nanocomposite were well fitted with the Langmuir model. Impressively, the maximum adsorption capacities towards rhodamine B and malachite green were estimated to be 400.0 and 561.8 mg g^{-1}, respectively, far exceeding many previously reported adsorbents. Moreover, the adsorbent could be easily regenerated by washing with ethylene glycol (EG), suggesting its excellent reusability. Even after 5 cycles of reuse, no obvious capacity degradation was observed. Furthermore, practical application of the magnetic adsorbent was demonstrated by the removal of organic dyes from domestic wastewater with a superior removal efficiency of higher than 97%.

Key Words: Magnetic adsorbent; Acid resistance; Organic contaminants; Water purification

1 Introduction

With increasing industrial development, various environmental problems have caused a great negative impact on human survival and development[1–8]. Water pollution is one of the most challenging environmental issues, which not only causes serious environmental and ecological damage, but

also threatens human health. Organic dyes are one kind of the most extensively existed in organic contaminants, which are widely used in various industries, such as textiles, paper, tannery, plastics, and paints[2–9]. It is estimated that more than 700000 tons of organic dyes are produced every year, around 10%–15% of which are released into environment[8]. Not only deterioration in water quality, but also adverse effects on

human health would be caused by these dyes. Consequently, considerable attentions have been paid to the detection, enrichment and removal of these dye pollutants in wastewater in recent years. Among various wastewater treatment techniques (including photocatalytic degradation, precipitation, oxidative degradation and adsorption), adsorption by various porous adsorbents is one of the most efficient, economical, and easy-handling strategies. Diverse adsorbents have been developed and used for the removal of organic dyes, including activated carbon, porous silica, zeolite and porous polymers[2–9]. Activated carbon is one of the most extensively used adsorbents, because of its high specific surface area, porosity, and nontoxicity. However, the separation and recovery of activated carbon from water after the adsorption process remains a concern because the activated carbon is usually in powdered or granular form[5,6].

Recently, it was proven that the incorporation of magnetic material into adsorbents was beneficial for fast separation and convenient recovery of these adsorbents[8–15]. The magnetic separation will not only simplify the separation process, but also reduce the energy consumption by avoiding complicated separation steps, such as filtration, precipitation and centrifugation. A magnetic graphene/iron oxide nanocomposite (G/Fe$_3$O$_4$) was prepared by Lu's group and demonstrated excellent performance for adsorption and separation of rhodamine B and malachite green from aqueous solutions[8]. However, common magnetic nanoparticles, including metal particles and metal oxides of Fe, Co, Ni and Mn, are unstable and prone to dissolution in acid environment, thus limiting their practical applications in acidic condition. Therefore，it is highly imperative to develop a novel magnetic adsorbent that is stable in acid environment, not only to simplify the separation process, but also to expand its application range. In the present work, a typical metal-organic framework (MOF), zeolitic imidazolate framework material (ZIF-67) was used as both template and precursor for the preparation of an acid-resistant magnetic Co/C nanocomposite[14,16]. Upon calcination at high temperature in inert atmosphere, the generated Co nanoparticles were uniformly wrapped by graphite layers, due to the graphitization of carbon under the catalysis of Co. The formed graphite layers could protect the Co particles from oxidation and acid environment, thus resulting in the generation of an acid-resistant magnetic adsorbent that could be applied in a wide pH range (pH 1–13). Impressively, the as-synthesized magnetic Co/C nanocomposites demonstrated excellent adsorption performance towards two typical organic dyes (rhodamine B and malachite green) over a wide pH range.

2　Experimental

2.1　Instruments and reagents

Cobalt nitrate (Co(NO$_3$)$_2$·6H$_2$O) and 2-methylimidazole were purchased from Aladdin Regeants Co. Ltd (Shanghai, China). Methanol was bought from Beijing Chemical Works (China). All these reagents were used as received without further purification. The deionized water (18.2 MΩ cm) was purified by Milli-Q system (Millipore Co., USA).

The X-ray diffraction (XRD) patterns were recorded on a D8 ADVANCE (Germany) using Cu-Kα (0.15406 nm) radiation. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG ESCALAB MKIIX-ray photoelectron spectrometer. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were collected on a Hitachi H-8100 TEM system. UV-Vis absorption spectra were collected on CARY 500 UV-Vis-NIR spectrophotometer.

2.2　Synthesis of materials

In a typical synthesis of ZIF-67, 24.38 g of 2-methylimidazole and 24.56 g of Co(NO$_3$)$_2$·6H$_2$O were dissolved into 1 L of methanol, respectively. Then, the two solutions were mixed together and stirred for a few minutes. After being stored at room temperature for 24 hours without any disturbance, the formed purple powders at the bottom were collected by centrifugation and washed with methanol for several times. The obtained purple powders were dried at 110 ºC.

During the carbonization process, the dried ZIF-67 was heated to 800 ºC at a heating rate of 5 ºC min^{-1} and maintained at this temperature for 1 h under Ar atmosphere. After cooling down to room temperature, the magnetic black powder was treated by 6 M HCl for 12 hours to remove the unstable metal particles and metal oxides. The resultant black powder was washed with deionized water for several times to remove any impurities and then dried at 110 ºC to obtain the magnetic Co/C nanocomposite.

2.3　Adsorption experiments

Aqueous solutions with different concentrations of dyes were treated by magnetic Co/C nanocomposites to remove the dyes. The mixtures were shaken vigorously for a period of time, and then separated by an external magnetic field. The concentrations of dyes before and after the treatment were monitored by UV-Vis absorption spectra. The removal efficiency was estimated according to changes of dye concentrations before and after the treatment. The adsorption capacity at equilibrium (q_e, mg g^{-1}) was calculated by the following equation:

$$q_e = (C_i - C_e)V/m \qquad (1)$$

where, V is the volume of the treated solution (mL), m is the weight of used adsorbent (g), and C_i and C_e are the initial concentration and final equilibrium concentration of dyes, respectively. All the adsorption experiments were carried out at room temperature.