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Microwave-assisted rapid synthesis of Mn_3O_4/ACF hybrid for high efficient As(V) removal

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ABSTRACT

In this paper, an efficient adsorbent, manganese-modified activated carbon fiber (Mn_3O_4/ACF), was rapidly fabricated by microwave-assisted hydrothermal treatment strategy, which is used to remove As(V) from simulated wastewater. The adsorbent was characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and N_2 sorption (BET). The characterization results showed that flake-like Mn_3O_4 particles in sizes of about 250 nm × 250 nm were homogeneously anchored on the surface of ACF. The goal of high As(V) removal efficiency was achieved with maximum adsorption capacity of $46.10\,mg\,g^{-1}$. The effects of temperature on thermodynamics and kinetics of As(V) adsorption were systematically studied. It was found that the adsorption of As(V) on the surface of Mn_3O_4/ACF is an endothermic process with a standard enthalpy change (ΔH^0) of $42.72\,kJ\,mol^{-1}$. Batch experimental result showed that almost all of the As(V) with initial concentration of $6.0\,mg\,L^{-1}$ can be removed in the presence of Mn_3O_4/ACF, where the residual As(V) in filtrate is less than $0.01\,mg\,L^{-1}$, below the tolerance level of drinking water suggested by World Health Organization (WHO). The presence of salt such as NaCl, Na_2SO_4 and $MgSO_4$ shows little effect on the adsorption of As(V), indicating the promising application of Mn_3O_4/ACF in industrial wastewater treatment.

1. Introduction

Arsenic, a well-known element, is ubiquitous in the environment and of worldwide serious concern due to its high toxicity and carcinogenicity (Smedley and Kinniburgh, 2002; Mandal and Suzuki, 2002; Matschullat, 2000; Ng et al., 2003). Arsenic compounds can be found in a wide range of aqueous environments such as waste water from the non-ferrous metals industry, acid waste mine drainage, and natural waters. The biggest challenge of water polishing is the ultra-low Arsenic concentration requirements set by environmental organizations around the world. To minimize these health risks, a strict guideline limit of $10\,\mu g\,L^{-1}$ set by the World Health Organization (WHO) has been adopted as the drinking water standard by many countries (W.H.O., 2004). The lowering of this MCL (maximum contaminant level) makes it necessary to find novel technologies to meet the regulation. Enhanced coagulation, membrane filtration, ion exchange and adsorption are technologies that have received much attention in recent years. In general, adsorption is considered to be more effective and efficient than membrane filtration. Moreover, adsorption is suitable for removal of low-level contaminants and adsorption processes need not produce sludge as with coagulation (Schnoor, 1997).

Considering that manganese oxides are effective in arsenic removal owing to the high affinity between manganese oxides and arsenic species, Sun et al. (2013) studied the property of manganese-modified ACF in As(V) removal. It was found that the adsorption capacity of Mn-ACF for As(V) was ranging from 23.77 to $36.53\,mg\,g^{-1}$, which was approximately 70 times higher than that of raw ACF. However, intimate contact between ACF and manganese oxides (MnO_x) nanosheets has not been achieved due to their large lattice mismatches and poor affinities. Thus, when depositing manganese oxides on the surface of

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ACF, it can grow only at the defect sites and tend to form a discontinuous island-like domain array to minimize the unfavorable ACF-oxide interfaces. Therefore, fabrication of MnO_x/ACF hybrid by homogeneous depositing a continuous and conformable MnO_x layer on ACF remains a great challenge and highly desired.

Microwave-assisted fabrication of manganese oxides can reduce the time required for the synthesis and increase the crystallinity of the product. Solvents which are polar in nature have a good potential to adsorb microwaves and convert them to thermal energy, resulting in the homogeneous nucleation and deposition when compared with conventional heating. Recently, the study of Tompsett et al. (2006) showed that when microwave-assisted heating is utilized, the synthesis duration is reduced by over an order of magnitude. In addition, the synthesized material has a more uniform dimension and composition.

Based on these considerations mentioned above, MnO_x modified ACF was rapidly synthesized by microwave-assisted heating treatment of the mixed solution of $MnSO_4$ and surface oxidized ACF. The formed MnO_x particles were found to homogeneously deposited on the surface of ACF. The performance of manganese oxides modified ACF was evaluated by adsorption of As(V) from simulated wastewater.

2. Experimental

2.1. Materials

Both $Na_3AsO_4{\cdot}12H_2O$ and $MnSO_4$ were purchased from Shanghai Chemical Reagent Co., China. ACF in thickness of 2 mm was from Nantong Senyou Carbon Fiber Co., Ltd., Nantong, China. All other chemicals used were of analytical reagent grades, and deionized (DI) water was used throughout all of the experiment.

2.2. Sample preparation

Before starting the deposition of manganese oxide nanosheets, ACF was thoroughly washed with DI water and oxidized with HNO_3. Specifically, 100 mL of 75 wt.% HNO_3 solution containing 5.0 g of dried ACF (2 cm × 2 cm) was firstly kept at 60 °C under magnetic stirring for 2 h. Then the oxidized ACF was rinsed by DI water until the filtrate was neutral.

After drying, 0.5 g of oxidized ACF were mixed with 100 mL of $MnSO_4$ solution (20 wt. %) at room temperature, which was transferred into a Teflon reactor uncovered. The mixed solution was heated for 3 min under microwave radiation (WXJ-III) of 900 W. After cooling to room temperature, the sample was washed with DI water to remove residual $MnSO_4$, and the resulted manganese loaded ACF sample was dried in an oven overnight at 105 °C and the resulted manganese loaded ACF sample was activated in a tube furnace for 2 h at 650 °C.

2.3. Sample characterization

The morphology of the adsorbent was observed on a field emission scanning electron microscope (FESEM) (Hitachi, Japan) with an acceleration voltage of 20 kV. The specific surface area were determined using a NOVA 2200e Surface Area and Pore Size Analyzer (Quanta chrome Instruments Co., USA). X-ray photoelectron spectroscopy (XPS) measurements were done with a Kratos XSAM800 XPS system with Mg K-a source and a charge neutralizer, all the binding energies were referenced to the C1s peak at 284.8 eV of the surface adventitious carbon. The X-ray diffraction (XRD) patterns were obtained on a D8-advance X-ray diffractometer (German Bruker) using Cu Ka radiation at a scan rate of $0.02^{\circ} 2\theta\ s^{-1}$. The accelerated voltage and applied current were 15 kV and 20 mA, respectively.

Table 1 – Nitrogen sorption characterization results of the adsorbent.

Adsorbent	Specific surface area ($m^2\ g^{-1}$)	Average pore size (nm)	Pore volume ($cm^3\ g^{-1}$)
ACF	1023	2.38	1.10
Mn_3O_4/ACF	861	2.23	0.45

2.4. Adsorption kinetics

0.05 g of manganese oxides modified ACF was added into 100 mL of As(V) solution (6.0 mg L^{-1}, pH = 7) and then shaken at certain temperature (298 K, 308 K, or 318 K). At given intervals of adsorption, small aliquots were withdrawn by a syringe, and filtered through a membrane (pore size 0.45 μm). The concentration of As(V) was measured with a Varian, Vista-Pro CCD simultaneous inductively coupled plasma ICPOES spectrophotometer.

2.5. Adsorption isotherm

0.05 g of manganese oxides modified ACF was added into 100 mL of As(V) solution (0.5–60.0 mg L^{-1}, pH = 7). After shaken for 100 min at certain temperature (298 K, 308 K, or 318 K) to establishment the adsorption–desorption equilibrium, the solution was filtered. The concentration of As(V) in filtrate was measured similar to the procedure for adsorption kinetics.

3. Results and discussion

3.1. Morphology

Fig. 1 shows the SEM image of ACF. It can be seen that ACFs are composed of bundles of threads (Fig. 1a). Magnified SEM image of a single thread showed that the diameter of the single fiber is about 10 μm, and the surface of the fiber is very smooth (Fig. 1b). After modified by manganese oxides, the surface of ACF becomes relative coarse (Fig. 1c). Careful view shows that the coarse surface of ACFs was caused by the homogeneous deposition of manganese oxides nanosheets in sizes of 250 nm × 250 nm (Fig. 1d). According to the analysis of ICP, the loading amount of manganese on the surface of ACF was about 25.5 wt%.

3.2. Nitrogen sorption

Table 1 compares the BET specific surface area, average pore size and pore volume of ACF before and after loaded with manganese oxides. It can be seen that the BET surface area decreases from 1023 to 861 $m^2\ g^{-1}$, and pore volume decreases from 1.10 to 0.45 $cm^3\ g^{-1}$ after modification of ACF by manganese. The decreased BET surface area and pore volume can be ascribed to the pore blockage and filling effect during ACF modification. Similar results were also reported by Maroto-Valer et al. during impregnation of oxidized AC with Fe and Cu (Maroto-Valer et al., 2004). They showed that with oxidation and impregnation, both surface areas and pore volumes decreased due to partial or complete pore blockage with oxygen complexes. Note that the average pore size of ACF was kept unchanged (Table 1), consistent with the results obtained by Okan et al. (2011).