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Hierarchically structured polyacrylonitrile nanofiber mat as highly efficient lead adsorbent for water treatment

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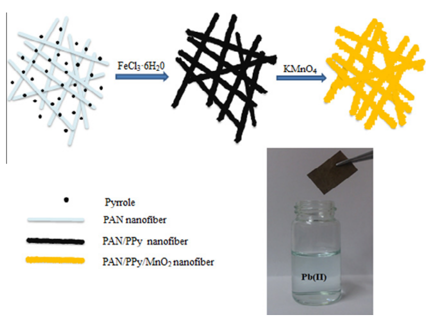
HIGHLIGHTS

- Hierarchical PAN/PPy/MnO_2 nanofiber was prepared.
- Hierarchical PAN/PPy/MnO_2 nanofiber mat was used to remove Pb(II).
- Adsorption capacity for Pb(II) is 251.90 mg/g.
- Adsorption performance remained up to 80% within 5 times cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Hierarchical nanofiber mat (polyacrylonitrile/polypyrrole/manganese dioxide, PAN/PPy/MnO_2) was prepared by electrospinning and followed by in situ polymerization of pyrrole monomer, and subsequently treated with $KMnO_4$ solution to deposit MnO_2. The obtained nanofiber mats were used as adsorbent for Pb(II) removal from aqueous solution. Fourier transform infrared (FTIR) results confirmed the presence of polypyrrole (PPy) and manganese dioxide (MnO_2) layers on the surface of PAN nanofiber. The morphology and structure of the PAN/PPy/MnO_2 nanofiber mat were studied by scanning electron microscopy (SEM) and transmission electron microscope (TEM). The hierarchical structures can be clearly seen from the SEM and TEM results. Thermo-gravimetric analysis (TGA) results showed that MnO_2 accounts for about 9.25 wt.% in the PAN/PPy/MnO_2 nanofiber. Adsorption results indicated that the adsorption performance for Pb(II) increased as the initial solution pH increased. The adsorption equilibrium reached within 120 min, and the process can be better described using the pseudo-second-order model. Isotherm data fitted well to the Langmuir isotherm model. Thermodynamic study revealed that the adsorption process is endothermic and spontaneous in nature. Desorption results showed that the adsorption performance can remain up to 80% after 5 times usage. The adsorption mechanism was also studied by XPS.

1. Introduction

As a result of rapid industrial development, environmental pollution becomes a serious problem for ecology [1]. Heavy metal ions are major pollutants of some ground and surface waters. Lead ions is one typical wide spread heavy metal contamination due to its extensive and wide applications in industrial processes, such as the production of mining, chemical, oil refining, electroplating,

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battery manufacturing and leather tanning, etc [2–4]. Pb(II) is a non-essential toxic metal showed several bio-toxic effects on organisms including humans even at extremely low concentrations. The maximum permissible limit of Pb(II) in drinking water was as low as 10 μg/L demonstrated by the World Health Organization [5]. Lead poisoning in human was caused severe damage to the kidney, nervous system, reproductive system, liver and brain [6]. Therefore, it is essential to remove Pb(II) from drinking water or lower the concentration of Pb(II). Several technologies have been developed for the removal of Pb(II) from water, such as precipitation, electroplating, ion exchange, membrane separation, coagulation, adsorption, etc [7–15]. Compared to other methods, adsorption is simple, economical and effective.

Currently, nano-sized metal oxide adsorbents were used for the removal of heavy metal toxic ions, including nanoparticles of ferric oxides, manganese oxides, aluminium oxides, titanium oxides, magnesium oxides and cerium oxides [16–22]. Due to its high adsorption capacity and selectivity, manganese oxides and their modifications were widely used to remove heavy metals ions and other harmful matters, such as Pb(II), Cu(II), Cs(I), Cd(II) and some organic dyes [23–28]. However, for small size, nano-sized metal oxide adsorbents are easily aggregated and need a next separation process from the solution, which weakened their adsorption capacity and increased the operation cost. In order to avoid this problem, some researchers use polymer fiber mat as the adsorbent. For example, the natural polymer chitosan which contains much amino groups was investigated for the removal of Cu(II) and Pb(II) after being spun to nanofiber mats [29]. Many kinds of aminated nanofiber mats were studied for Cu(II), Pb(II), Fe(II), Ag(I) removal performance [30–33]. In our previous work, PAN/PANI and PAN/PPy core/shell nanofiber mats have been prepared and used for Cr(VI) ions removal from aqueous solutions [34,35]. As reported by the literatures, due to their reducibility came from the positively charged nitrogen atoms [36,37], pyrrole and aniline were widely used to reduce high valence of Mn compounds to prepare kinds of PANI/MnO_2 and PPy/MnO_2 composites [38–41]. However, those composites were mainly used for supercapacitor.

Inspired by the above work, we fabricated a new hybrid adsorbent by coating nano-sized hydrous manganese oxides onto the surface of PAN/PPy core/shell nanofiber by a facile adsorption method. Hence, the obtained PAN/PPy/MnO_2 triaxial nano-cable was used to remove Pb(II) from aqueous solution. And it can be easily separated after adsorption. To further evaluate its adsorption performance, solution pH, contact time, and temperature were examined. The adsorption kinetics and thermo-dynamics of the adsorption process were also investigated. Moreover, the reusability of this newly developed adsorbents and the underlying adsorption mechanisms were studied.

2. Experimental

2.1. Chemicals

Polyacrylonitrile (M_w = 150,000) was purchased from Sigma–Aldrich. Dimethylformamide (DMF), sodium chloride (NaCl), lead nitrate [$Pb(NO_3)_2$], copper nitrate [$Cu(NO_3)_2$], nickel nitrate [$Ni(NO_3)_2$], potassium permanganate ($KMnO_4$), Iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) were purchased from Sinopharm Chemical Reagent Co. Ltd. Pyrrole (Py, 98+%) was purchased from Alfa Aesar.

2.2. Preparation of PAN/PPy and PAN/PPy/MnO_2 nanofiber mat

The PAN/PPy core/shell nanofiber mat was prepared via electrospinning followed by in situ polymerization of pyrrole monomer. The exhaustive methods were reported in our published paper [34]. MnO_2 was spontaneously deposited onto the surface of PAN/PPy nanofiber through a direct redox reaction between the PPy and MnO_4^{-1}. In a facile and typical route, a piece of PAN/PPy nanofiber mat was added to a 50 mL beaker which contains 30.0 mL of 200 mg/L $KMnO_4$ solutions. And the reaction solution was shaken in a thermostatic shaker bath, operating at 25 °C, and 100 rpm for 12 h. Finally, the PAN/PPy nanofiber mat was taken out, washed with deionized water repeatedly to remove the residual MnO_2 particles, and then dried in vacuum overnight.

2.3. Adsorption experiments

$Pb(NO_3)_2$ was used as the source of Pb(II), 10.0 mg dry PAN/PPy/MnO_2 nanofiber mat was directly added into a beaker containing 12.0 mL 200 mg/L Pb(II) solutions with pH value of 6.0 for 12 h. During this process, the beaker was shaken in a thermostatic shaker bath, operating at 25 °C and 100 rpm. 0.1 M HNO_3 and 0.1 M NaOH were used to adjust the pH of the Pb(II) solution. The removal percentage of Pb(II) can be calculated by the following equation:

$$\%\ \text{removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration of Pb(II) in solution (mg/L) and C_e is the equilibrium concentration (mg/L).

The adsorption isotherms for Pb(II) were established by batch adsorption experiments. 10.0 mg PAN/PPy/MnO_2 nanofiber mat was immersed into 12.0 mL Pb(II) solutions with different initial concentrations ranging from 50 mg/L to 400 mg/L. The initial pH value of the Pb(II) solution was adjusted to 6.0. The adsorption was carried out at 25 °C with constant shaking, and then kept for 12 h to establish adsorption equilibrium. The equilibrium adsorption amount was determined using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 is the initial concentration of Pb(II) in solution (mg/L), C_e is the equilibrium concentration (mg/L), q_e is the equilibrium adsorption amount (mg/L), m is the mass of adsorbent (g), and V is the volume of solution (L).

The kinetic adsorption performance was studied by contacting 10.0 mg of PAN/PPy/MnO_2 nanofiber mat with Pb(II) solutions of different initial concentrations at 25 °C. The initial pH value of the Pb(II) solution is 6.0, and the solution was shaken in a thermostatic shaker bath during the process. Samples were taken out of the solution at different time, each time 50 μL. The adsorption amount was calculated by the following equation:

$$q_t = \frac{(C_0 - C_e)V}{m} \quad (3)$$

where q_t is the adsorption amount at time t, C_0 is the initial concentration of Pb(II) in solution (mg/L), C_t is the Pb(II) concentration at time t (mg/L), m is the mass of adsorbent (g), and V is the volume of solution (L).

2.4. Desorption experiment

For desorption studies, 10.0 mg PAN/PPy/MnO_2 nanofiber mat was first contacted with 12.0 mL 200 mg/L Pb(II) for 12 h at 25 °C. Then the adsorbents were immersed into 12.0 mL 0.05 M, 0.10 M, 0.20 M HCl solution for 3 h at 25 °C. The above procedure was repeated for 5 times to test the reusability of the adsorbents.