Electronic Supplementary Information (ESI)

The title: Preparation of novel poly (vinyl alcohol)/SiO\(_2\) composite nanofiber membranes with mesostructure and their application for removal of Cu\(^{2+}\) from waste water

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Reagents and materials

3-Mercaptopropyltrimethoxysilane (MPTMS, 99%) was procured from Aldrich. Tetraethyl orthosilicate (TEOS), cetyltrimethyl ammonium bromide (CTAB), absolute ethylalcohol and poly (vinyl alcohol) (PVA, 99%, high molecular weight, MW 88000–97000) were provided by Sinopharm Chemical Reagent Company, China. Nitrate of copper was used to prepare the heavy metal ion solution. Deionized (DI) water was used throughout this work.

Preparation of PVA/SiO\(_2\) gels

A silica gel, with the molar composition TEOS : CTAB : MPTMS : HCl : H\(_2\)O : Ethanol = 1 : 0.31 : 0.188 : 0.025 : 15 : 5 was prepared by hydrolysis polycondensation. First, 2.19 g CTAB was dissolved in 7.37 g ethanol and vigorously stirred for 0.5 h at 60 °C. Second, 8.64 g DI water, 1.54 g MPTMS were added into the mixture and further stirred for 0.5 h at 60 °C. Then, 6.64 g TEOS was slowly added into the solution mixture. Finally, 0.8 ml HCl (2mol/L) was dropped slowly into the mixture and the SiO\(_2\) gel was obtained for 2 h at 30 °C. 10.0 g 10 wt % PVA solution was dropped slowly into the silica gels, then the reaction proceeded in a water bath at 60°C for another 4 h. Thus, a viscous gel of PVA/SiO\(_2\) composite was obtained.

Preparation of nanofiber membranes

The above PVA/SiO\(_2\) composites were contained in a plastic capillary. A copper pin connected to a high-voltage generator was placed in the solution. A grounded iron drum, covered with an aluminium foil, served as a counter electrode. A voltage of 20 kV, at a speed of 0.5ml.h\(^{-1}\) was applied to the solution and a dense web of fibers was collected on the aluminium foil. These fibers were dried initially for 12 h at 60 °C under vacuum. Then the electrospun PVA/SiO\(_2\) fibers membrane was refluxed in ethanol/HCl (molar ratio of 10:1) for 24 h at 70 °C to remove the template, and finally dried for 6 h at 60 °C under vacuum.
Characterization

Transmission electron micros copy (TEM) images were taken using a JEM-2011 electron microscope operating at 200 kV. Scanning electron microscopy (SEM) images were recorded with a field emission XL-30 SEM. Fourier transform infrared spectroscopy (FTIR) of KBr powder-pressed pellets was recorded on a BRUKER VECTOR 22 spectrometer. The N\textsubscript{2} adsorption-desorption isotherm measurements were taken with a Quantachrome NOVA1000 system. Wide-angle x-ray diffraction (WARD) patterns of the samples were recorded using a Philips diffractometer with a Geiger counter. Scans were made from 10\degree to 90\degree (2\theta) at the speed of 2.\degree/min. The concentrations of Cu\textsuperscript{2+} remaining in the solutions were analyzed by an Inductively Coupled Plasma Spectrometer (ICP, Optima 2100 DV, America).

The adsorption and desorption isotherm on the nanofiber membranes

Adsorption experiments were conducted as follows. For each 250 ml conical flask, approximately 50 mg of nanofiber membranes and 100 ml of Cu\textsuperscript{2+} solution, each with different concentrations (0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 7.0 and 10.0 mmol/L, respectively) were added. Dilute nitric acid and sodium hydroxide solutions were used to adjust the initial pH value to 5. The oscillation treatment consisted of oscillations at 200r/min at a temperature of 303 K for 60 min. Then, the suspension was separated using a 0.45 µm Uniflo filter. The filtrate was determined for Cu\textsuperscript{2+} concentration by using ICP/OES spectroscopy. The fibers were separated by filtration and rinsed with DI water to remove residual solution trapped among the fibers. Then the PVA/SiO\textsubscript{2} nanofibers with adsorbed copper ions transferred to a flask with either 100 ml of 1 mol/L HCl solution or DI water (pH 5.0). The flask was shaken at 200r/min in a rotary shaker at 293K, and the copper ion concentrations in the solution were analyzed over time. ICP/OES spectroscopy was used to determine the copper concentration in the samples.

Regeneration for nanofiber membranes

About 100 ml of 1.0 mmol/L Cu\textsuperscript{2+} solution was added to a 250 ml conical flask containing 50mg of nanofiber membranes. After an oscillation treatment for 60 min at a temperature of 293K, the suspension was separated using a 0.45 µm Uniflo filter. The filtrate was determined for Cu\textsuperscript{2+} concentration by using ICP/OES spectroscopy. The copper-loaded adsorbent was then stirred in
100 ml of 1 mol/L HCl solution for 2 h at room temperature to strip the Cu$^{2+}$ ion. Then the suspension was filtered and the residue was added to 1 mol·L$^{-1}$ NaHCO$_3$ solution with a stirring time of 2 h at room temperature. After filtration and washing, the sample was neutralized to pH 7. The cleaned membrane was then dried in a vacuum oven at 60 °C. The first adsorption–desorption cycle was followed by five other cycles using the same adsorbent batch. After six regeneration cycles, the sample was dissolved using 100 ml dilute nitric acid for 3 h. The solution was then diluted to 500 ml to measure the Cu$^{2+}$ ion concentration using ICP/OES spectroscopy.