
Supporting Information

An Effective Mercury Ion Adsorbent Based on a Mixed- Matrix Polyvinylidene Fluoride Membrane with Excellent Hydrophilicity and High Mechanical Strength

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2. Experimental

2.1. Materials and characterization

Vermiculite was provided by Xinjiang Nonmetallic Minerals Xiazijie vermiculite Co., Ltd. 3-aminopropyl triethoxysilane (APTES) was purchased from Sigma-Aldrich. Polyvinylidene fluoride (PVDF) powder [Kynar 761] was provided from Arkema (Shanghai, China) and was dried at 100 °C overnight to eliminate the absorbed water. Polyethyl-enimine [PEI, Mw = 70000 Da, 50wt % aqueous solution, branched polymer (–NHCH₂CH₂–)_x[–N(CH₂CH₂NH₂)–CH₂CH₂–]_y], polyvinylpyrrolidone (PVP, K30), epichlorohydrin (ECH) and Na₂S₂O₈ were purchased from Aladdin Company. N, N-Dimethylformamide (DMF), mercury chloride (HgCl₂), cadmium chloride dehydrate (CdCl₂·2.5H₂O), lead nitrate (Pb(NO₃)₂) and copper nitrate (Cu(NO₃)₂·3H₂O) were purchased from Adamas (China). The reagents used in all experiments were of analytical grade, and ultrapure water (18.2 MΩ·cm) was used in all experiments.

FTIR spectra were recorded with a Fourier-transform infrared spectrometer (Nicolet iS5, Thermo, USA) in the spectra range of 400–4000 cm^{–1} with an attenuated total reflection (ATR) accessory. SEM measurements were conducted by field-emission scanning electron microscopy (SU8020, Hitachi, Japan). The X-ray photoelectron spectroscopy (XPS) measurements were performed on a multifunctional X-ray photoelectron spectrometer (PHI-5702, Perkin Elmer, USA) with Al Kα radiation as the excitation source (14 kV). Variation in sample crystal structures with adsorption of Hg(II) was tracked by X-ray diffractometer (XRD) (D8 advance, Bruker, Germany) under Co Kα1 radiation ($\lambda = 1.5405 \text{ \AA}$) between 5° and 80° (2 θ). The wettability was determined from contact angle measurements using a contact angle analyzer (XG-CAMA, Xuanzhun, China). The tensile strength was obtained by using a universal testing instrument (C43-104, MTS, USA).

2.3. Adsorption tests of Hg(II) removal

Batch experiments were conducted to inspect the uptake behavior of Hg(II) ions on the PVDF/PEI in aqueous solutions within the pH range from 1.5 to 5.5 at 30 °C. In a typical experiment, 20 mg of the as-prepared adsorbent was put into a 100 mL capped conical flask with 20 mL of the desired concentration of Hg(II) solution (0.05 to 2000 mg/L). The mixture was mechanically shaken at a constant temperature of 30 ± 0.2 °C by the required time. After equilibration, the membrane was separated directly by fishing out and the residual Hg(II) ion in the aqueous was measured using atomic fluorescence spectrophotometer. All experiments were run in triplicate and the average was taken as the final result.

The selective adsorption was performed in a multi-component solution including Cu(II), Cd(II), Pb(II) and Hg(II) ions. The concentrations of Hg(II), Cu(II), Cd(II), and Pb(II) in the aqueous solution were 400.0 mg/L, respectively. After adsorption, the inductively coupled plasma atomic emission spectroscopy was used to determine the equilibrium concentration of Cu(II), Cd(II), and Pb(II) ions. Further experiments were performed by adding various anions (Cl[–], SO₄^{2–}, NO₃[–], H₂PO₄[–] and CH₃COO[–]) to the Hg(II) solution to analyze their effects on the adsorption.

The reusability of the adsorption membrane was evaluated carefully. The Hg(II)-loaded membrane was fetched out by using a tweezer and immersed into 20 mL of 2 mol/L HCl solution and shaken for 3 hours, then rinsed with water several times until the adsorbed acid was completely washed. After freeze-drying, the adsorbent was reused in the next cycle (400 mg/L Hg(II)).

The residual Hg was analyzed by an atomic fluorescence spectrophotometer (AFFS, 8330, Beijing Jitian) with a detection limit of 0.0013 µg/L. The other residual metal ion concentrations were determined by an inductively coupled plasma atomic emission spectrometer (7400 ICP-OES, Thermo Fisher, USA), and the detection limits for copper, cadmium, and lead ions were 0.005 mg/L, 0.001 mg/L, and 0.01 mg/L, respectively.

The adsorption capacity Q_e (mg/g) of PVDF/80%PEI toward the metal ions at equilibrium was calculated according to Eq. (1):

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

and the adsorption efficiency (E) was calculated by Eq. (2):

$$E = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L) of the metal ions in the solution, respectively, V (L) is the volume of the solution, and m (g) is the mass of the adsorbent.

K_d is the distribution coefficient of metal ions and was calculated by Eq. (3):

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

The high value of K_d indicated a large number of metal ions retained by the adsorbent, while a low value of K_d indicated that more metal ions still remained in the solution.

Adsorption kinetics

Pseudo-first-order model is given by:

$$Q_t = Q_f(1 - e^{-k_1 t}) \quad (4)$$

the pseudo-second-order model is given by:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_f^2} + \frac{1}{Q_f} t \quad (5)$$

where k_1 (1/min) and k_2 [g/(mg·min)] are the rate constants for the first-order and second-order models, respectively, Q_f is the fitted adsorption value (mg/g) at equilibrium, and Q_t is the experimental value (mg/g) at a set time t (min).

Adsorption isotherms

The Langmuir model is given by:

$$Q_e = \frac{Q_m b_L C_e}{1 + b_L C_e} \quad (9)$$

the Freundlich model is given by:

$$Q_e = K_F C_e^{1/n_F} \quad (10)$$

where Q_m is the theoretical maximum adsorption capacity (mg/g), C_e is the final equilibrium mercury concentration (mg/L), b_L is the Langmuir constant (L/mg) related to the adsorption strength, K_F is the Freundlich constant related to the adsorption strength (mg/g) (L/mg), n_F is the Freundlich constants related to the adsorption capacity, respectively.

3. Results and discussion

Table S1. The results of pollution resistance tests.

	J_0 (L/m ² ·h)	J_1 (L/m ² ·h)	m
PVDF/PEI membrane	25	1	0.96
Mixed matrix PVDF membrane	412	366	0.11

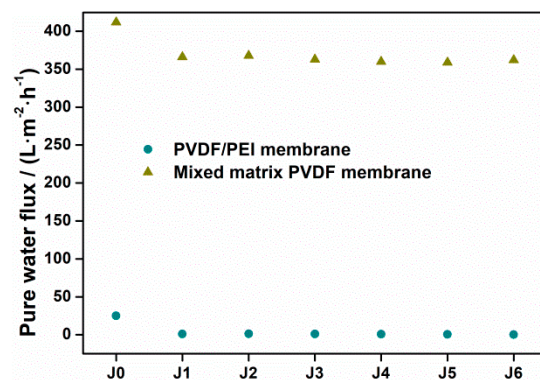


Figure S1. Pure water flux of PVDF/PEI membrane and mixed matrix membrane after different number of times of the immersion and drying occurred.

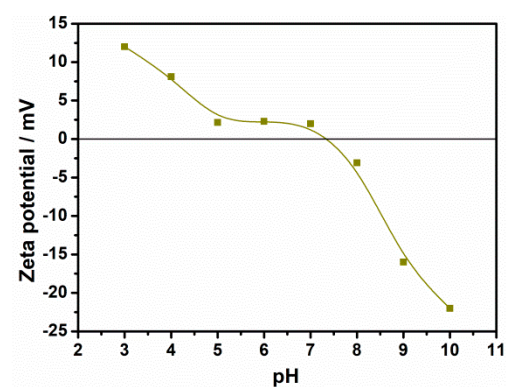


Figure S2. Relationship between Zeta potential of the mixed matrix membrane and pH.