Supporting Information for

In-situ synthesis of porous ZrO_2 coated fiber membrane for efficient static and dynamic removal of Se(IV)

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1. The details of the reagents and instruments

$Zr(NO_3)_4 \cdot 5H_2O$, NaOH, urea, HCl, HCHO, polyethylene glycol 400, N,N-dimethylformamide (DMF), polyvinyl pyrrolidone, cellulose acetate, ethanol, SeO_2, NaCl, $Zn(NO_3)_2$, $Cu(NO_3)_2$, $FeCl_3$, KCl, KNO_3, K_2SO_4, K_2CO_3, and K_3PO_4 were all purchased from Sinopharm Chemical Reagent Co., Ltd. Unless otherwise stated, all these chemicals and reagents were directly used without further purification. Deionized water was utilized throughout the study.

The as-prepared ZrO_2 and ZrO_2/FM were characterized by following instruments. X-ray diffraction (XRD) patterns were obtained on a 6100 diffractometer (Shimadzu, Japan). Scanning electron microscopy (SEM) measurements were performed on a JSM-7800F microscope (JEOL, Japan). The porous properties were determined by using a Micromeritics TriStar II 3020 analyzer (Micromeritics, USA). X-ray photoelectron spectroscopy (XPS) were performed on an ESCALAB-MKII spectrometer (Thermo-Fisher, USA). Zeta potential was measured by a NanoBrook Series size and zeta potential analyzers (brookhaven, USA).

2. The details of batch adsorption tests

The effect of the solution pH on the Se(IV)removal efficiency by using ZrO_2/FM was first studied. The pH of Se(IV)-containing solution was adjusted by 0.5 M NaOH and HCl. In detail, 10 mg ZrO_2/FM was added into 20 mL Se(IV)-containing solution (5.0 mg L^{-1}). Thereafter, the above solution was incubated in a 25 °C water bath for 1 h. The solution was purified through a 0.22 μm microfiltration membrane. The concentration of the remaining Se(IV) was determined by using inductively coupled plasma optical emission spectrometer (ICP-OES), and the Se(IV) removal efficiency by using ZrO_2/FM was calculated by the equation (1):

$$R\% = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where $R\%$ is the Se(IV) removal efficiency by using ZrO_2/FM and C_0 and C_t are Se(IV) concentrations in the initial and at the time t (mg L^{-1}), respectively.

The effect of contact time on the Se(IV) removal efficiency by using ZrO_2/FM was studied. In detail, 10 mg ZrO_2/FM was added into 20 mL Se(IV)-containing solution (pH 4.0, 5.0 mg L^{-1}). Thereafter, the above solution was incubated in a 25 °C water bath for different time. The Se(IV) removal efficiency by using ZrO_2/FM was calculated by the equation (1):

In addition, the captured amounts of Se(IV) at different time (Q_t) were calculated by the equation (2):

$$Q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where Q_t is the Se(IV) adsorption capacity at the time t (mg g^{-1}), W is the ZrO_2/FM mass (g), and V is the Se(IV)-containing solution volume (L).

The adsorption isotherms of Se(IV) with different initial concentration using ZrO_2/FM were studied. 0.01 g ZrO_2/FM was added into Se(IV)-containing solution (pH 4.0, Se(IV) concentrations ranging from 8 mg L^{-1} to 50 mg L^{-1}) and incubated for 1 h. The Se(IV) equilibrium adsorption amounts (Q_e) were calculated by the equation (3):

$$Q_e = \frac{(C_0 - C_e)V}{W} \quad (3)$$

where C_e is the equilibrium Se(IV) concentrations (mg L^{-1}).

The selectivity of ZrO_2/FM towards Se(IV) was also investigated. 10 mg ZrO_2/FM was added into 20 mL mixed solution containing 5.0 mg L^{-1} Se(IV) and 5.0 or 25.0 mg L^{-1} possible co-existing ions. The possible co-existing ions include Na^+, Zn^{2+}, Cu^{2+}, Fe^{3+}, Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}, and PO_4^{3-}. And the above solution was incubated for 1 h. And the Se(IV) removal efficiency was calculated by the equation (1).

3. The details of ZrO_2/FM performance evaluation

Firstly, the permeate flux of ZrO_2/FM was studied in this study. In details, pure water and Se(IV)-containing solution (5.0 mg L^{-1}) was driven through ZrO_2/FM under different pressures ranging from 20 ~ 100 KPa. Then, the pure water fluxes and permeate fluxes (F) under different pressures were calculated by the equation (4):

$$F = \frac{V}{S \times t} \qquad (4)$$

where V, S, and t are the pure water or permeate solution volume (L), ZrO_2/FM effective adsorption area (m^2), and the filtering operation time (h), respectively.

Additionally, the dynamic Se(IV) removal performance by using ZrO_2/FM was also investigated. In details, the as-prepared ZrO_2/FM was fixed in a sand core funnel and the Se(IV) solution in reservoir was introduced into the sand core funnel through the peristaltic pump. Then, the Se(IV) solution (5.0 mg L^{-1}) was driven through ZrO_2/FM under the 100 KPa pressure. And the Se(IV) removal efficiency was calculated by the equation (1).

Regeneration performance is one of most important indicators to the evaluation of ZrO_2/FM. Thus, the ZrO_2/FM regeneration performance was explored in the study. The used ZrO_2/FM was desorbed by immersing ZrO_2/FM in NaOH solution (0.5 M) for 1

h. All dynamic Se(IV) removal experiments were performed at room temperature and pH 4.0 under 100 KPa pressure (The initial Se(IV) concentration is 5 mg L^{-1}).

4. The details of adsorption kinetics and isotherm

The adsorption process is fitted by both pseudo-first-order and pseudo-second-order kinetic models. And the pseudo-first-order and pseudo-second-order kinetic models are displayed as equation (5) and (6):

$$Q_\mathrm{t} = Q_\mathrm{e}(1 - e^{-k_1 t}) \tag{5}$$

$$Q_\mathrm{t} = \frac{k_2 Q_\mathrm{e}^2 \mathrm{t}}{1 + k_2 Q_\mathrm{e} \mathrm{t}} \tag{6}$$

where k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constants of the pseudo-first-order and pseudo-second-order kinetic models, respectively.

Moreover, the Langmuir and Freundlich isotherm models are used to describe the Se(IV) adsorption process by using ZrO_2/FM, which can be displayed as equation (7) and (8):

$$Q_\mathrm{e} = \frac{Q_\mathrm{m} K_\mathrm{L} C_e}{1 + K_\mathrm{L} C_e} \tag{7}$$

$$Q_\mathrm{e} = K_\mathrm{F} C_\mathrm{e}^{1/\mathrm{n}} \tag{8}$$

where K_L (L mg^{-1}) is the Langmuir constant and K_F (mg g^{-1}) $(L\ mg)^{1/n}$ is the Freundlich constant.

5. The details of Thomas dynamic model

Thomas dynamic model was employed to calculate experimental data from fixed-bed column experiment. The mathematical model of Thomas model is presented as equation (9):

$$\frac{Ct}{C_0} = \frac{1}{1 + \exp\left[\left(\frac{K_{TH}}{Q}\right)(Q_e m - C_0 Q t)\right]} \tag{9}$$

Where K_{TH} is the Thomas adsorption rate constant (L mg^{-1} min^{-1}), V is the effluent volume (L), m is the ZrO_2/FM mass (g), and Q is the flow rate of influent (L·min^{-1}).

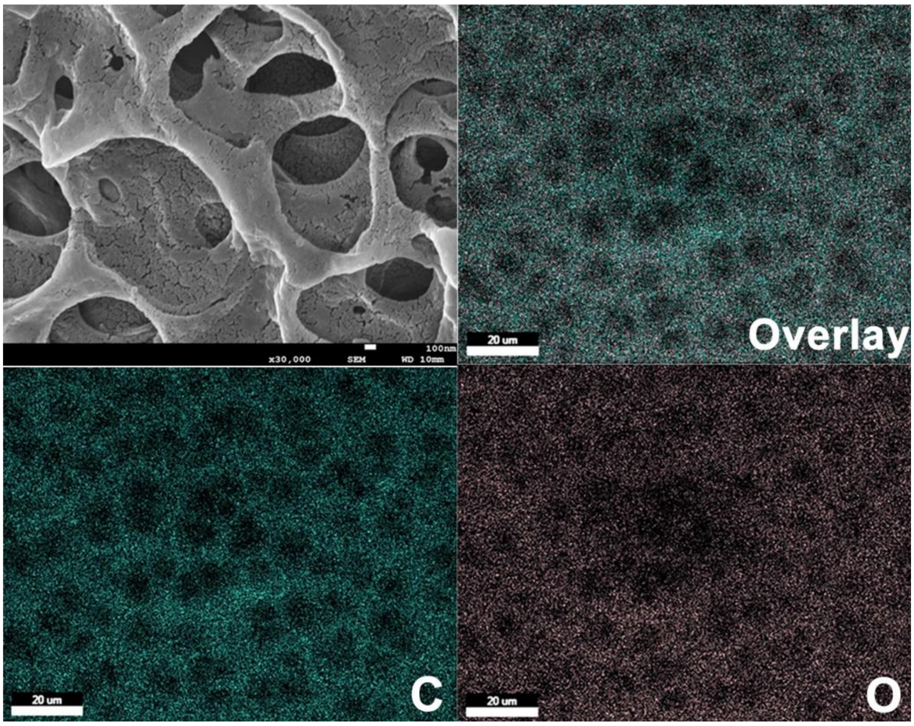

Fig. S1. Elemental mapping of pure FM.

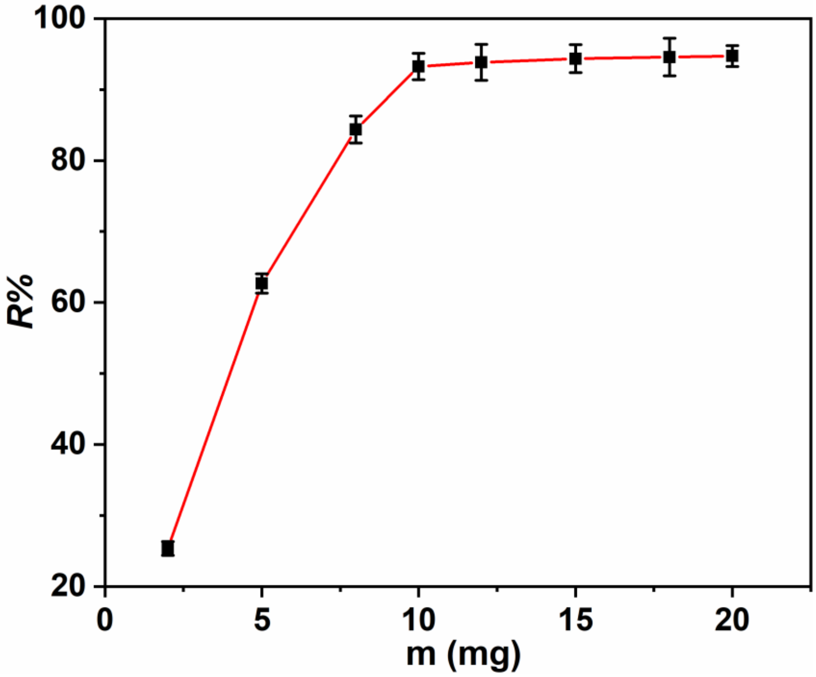

Fig. S2. Effect of ZrO_2/FM amount on the Se(IV) removal efficiency.

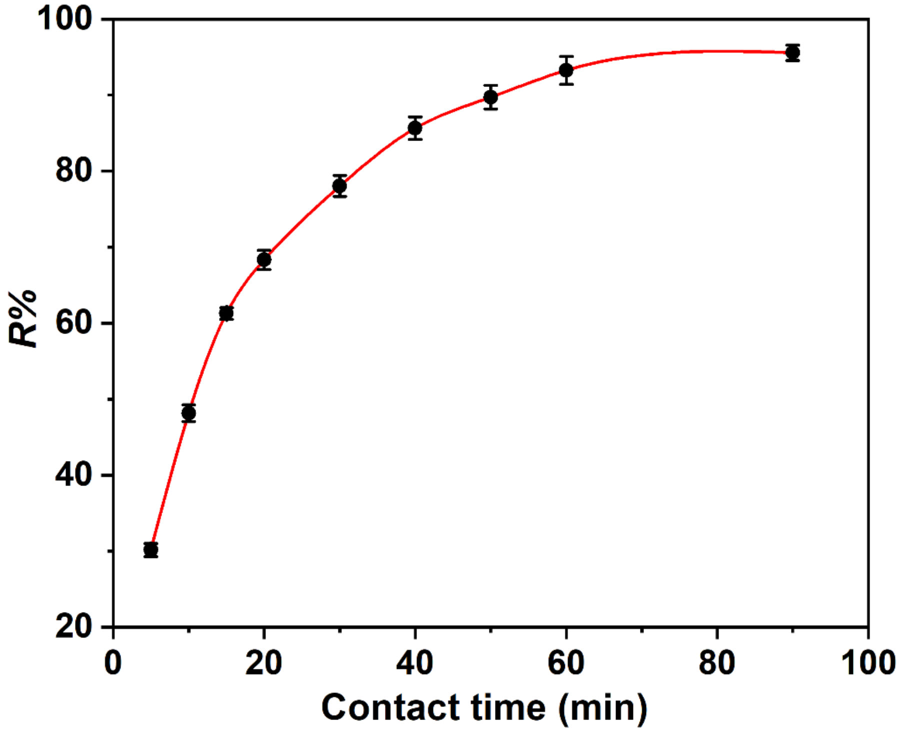

Fig. S3. Effect of contact time on the Se(IV) removal efficiency.

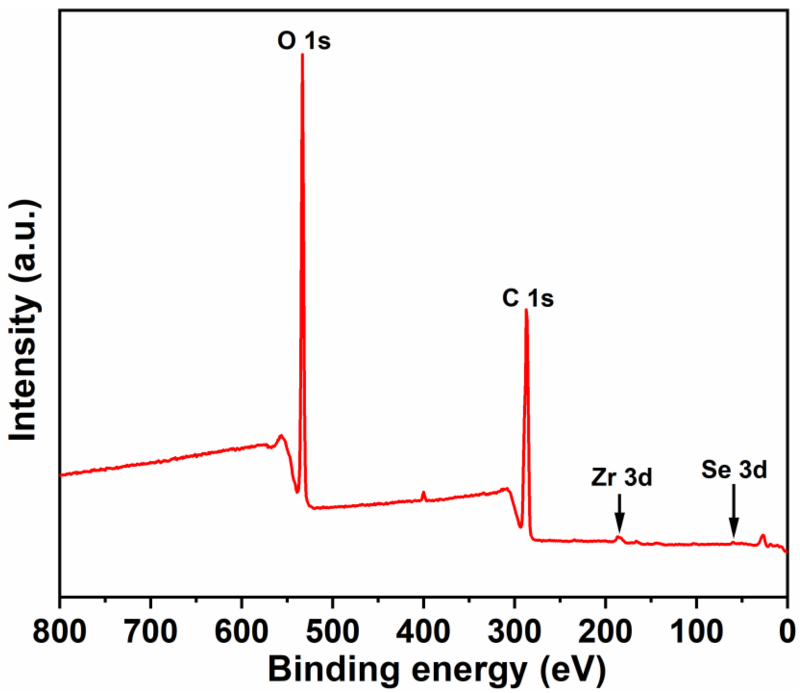

Fig. S4. Full XPS of ZrO_2/FM after removing Se(IV).

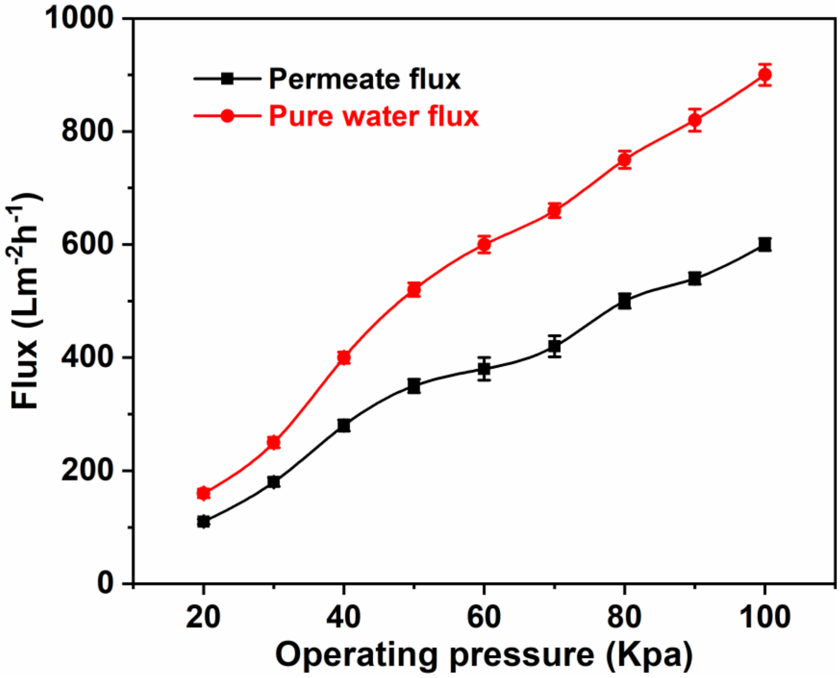

Fig. S5. Effect of operating pressure on pure water flux and permeate flux.

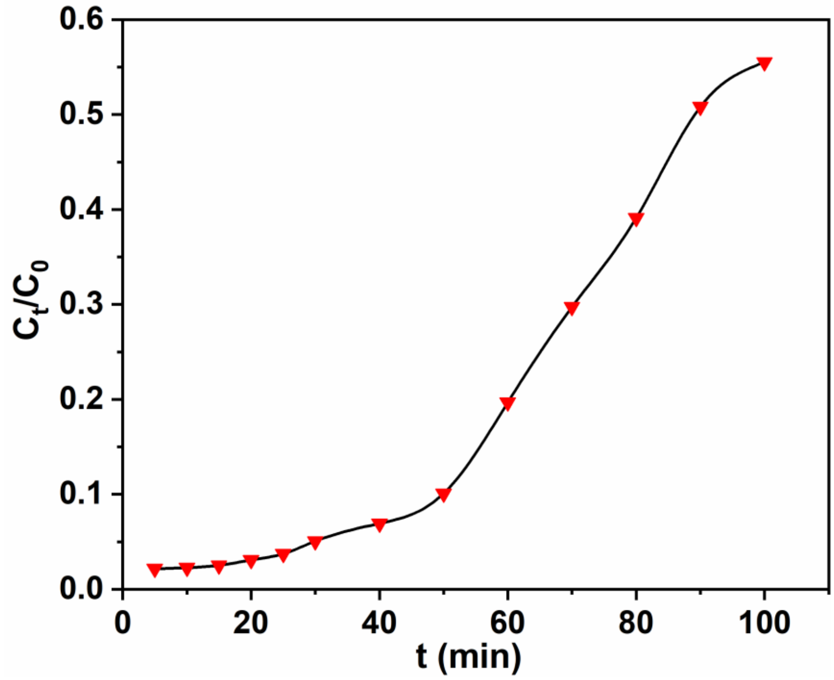

Fig. S6. Breakthrough curve of ZrO_2/FM at 100 Kpa pressure.