Supporting Information

L-cystine/L-cysteine Impregnated Nanofiltration Membrane with Superior Performance of Anchoring Heavy Metal in Wastewater

Hong-Li Zhang, [&,†] *Huaqiang Cai,* [&,§] *Yu Xia,*[†] *Pan Zhang,*[†] *Si-Wei Xiong,*[†] *Jing-Gang Gai*[*,†]

[†] *State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu, Sichuan 610065, P. R. China*

[§] *Institute of chemical materials, China academy of engineering physics, Mianyang 621900, PR China*

Supporting Figures and Tables

[*] Corresponding authors. Tel.: +86 28 85467166; fax: +86 28 85402465. E-mail addresses: gaijinggang@scu.edu.cn (J-G. Gai)

[&] These authors contributed equally to this work and should be considered co-first authors

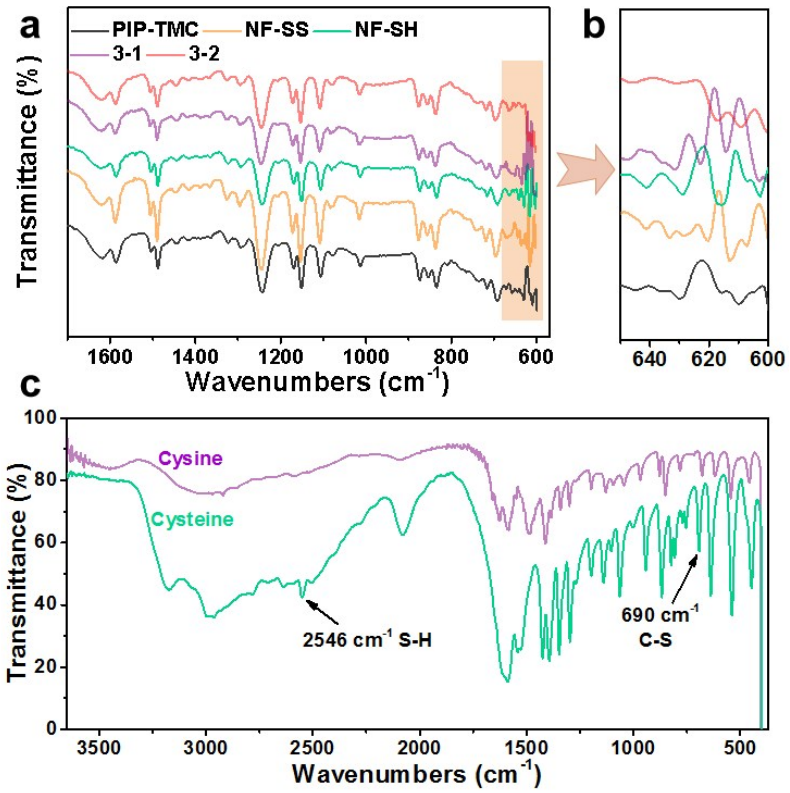

Figure S1 (a) FT-ATR spectra and (b) the enlarged view of PIP-TMC, NF-SS, NF-SH, **3-1** and **3-2** NF active layers; (c) FT-IR spectra of L-cystine and L-cysteine monomers.

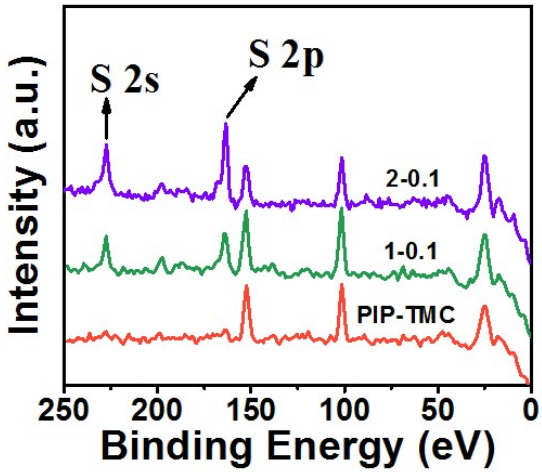

Figure S2 Enlarged XPS spectra of PIP-TMC, NF-SS, NF-SH active layers in the range of binding energy of 0~ 250 eV.

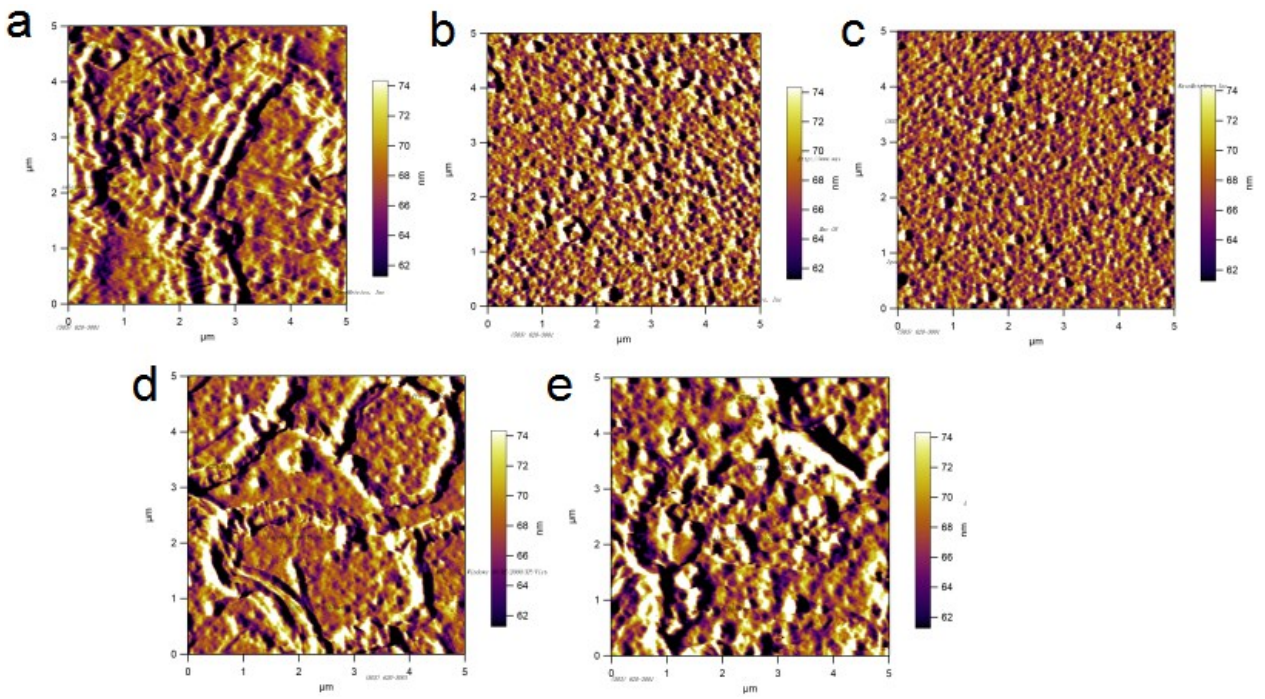

Figure S3 Suface-sectional AFM images of (a) PIP-TMC, (b) NF-SS, (c) NF-SH, (d) 3-1, and (e) 3-2 active layers, respectively.

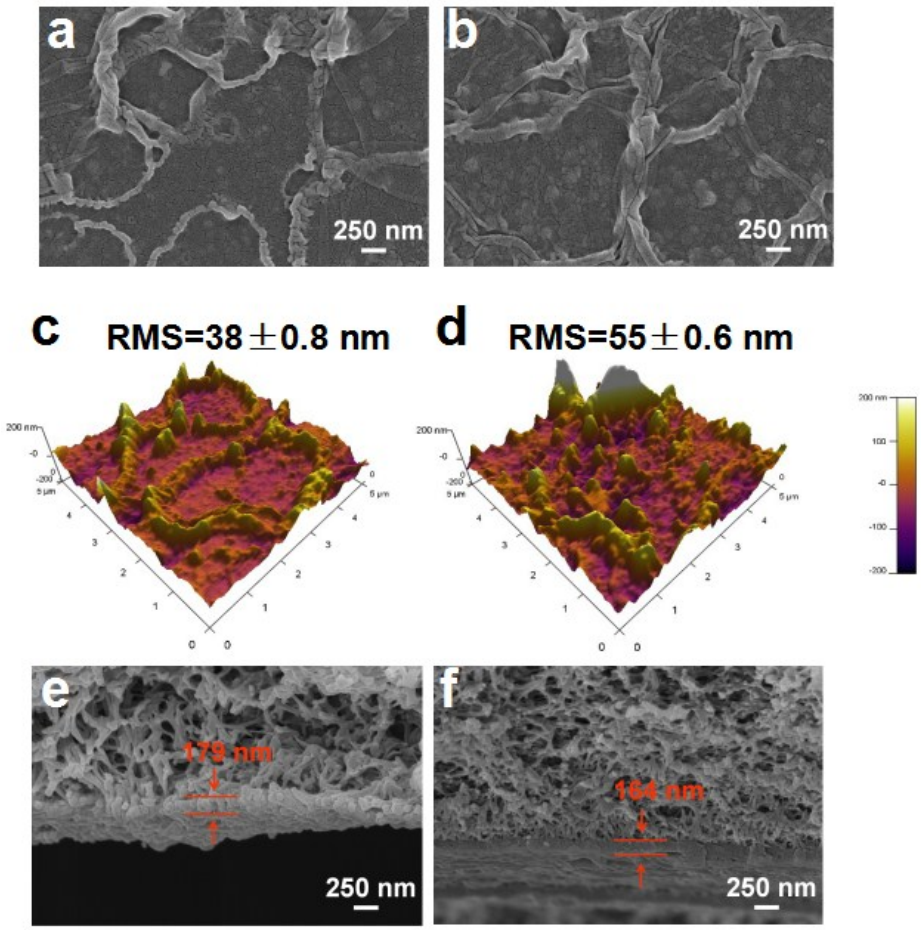

Figure S4 (a, b)The surface-sectional SEM, (c, d) AFM and (e, f) cross sectional SEM images of **3-1** and **3-2** active layers.

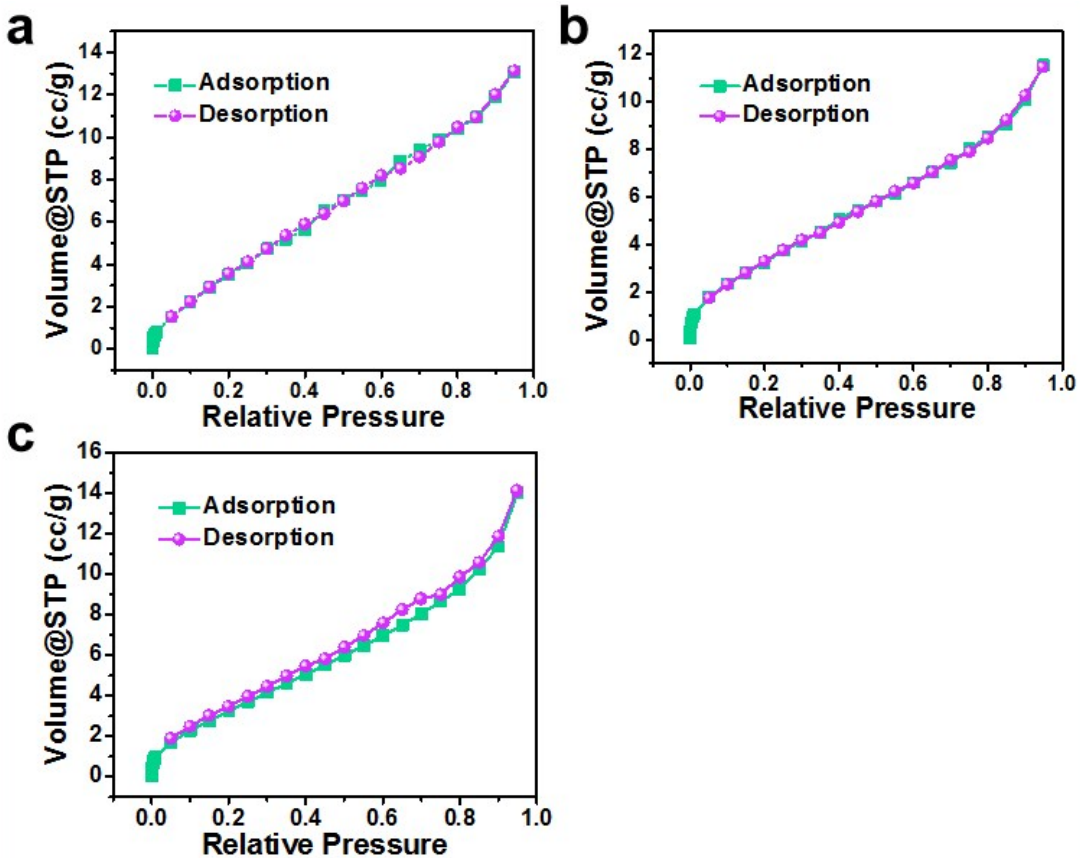

Figure S5 Nitrogen-sorption isotherm curves of (a) PIP-TMC, (b) NF-SS and (c) NF-SH measured at 77 K.

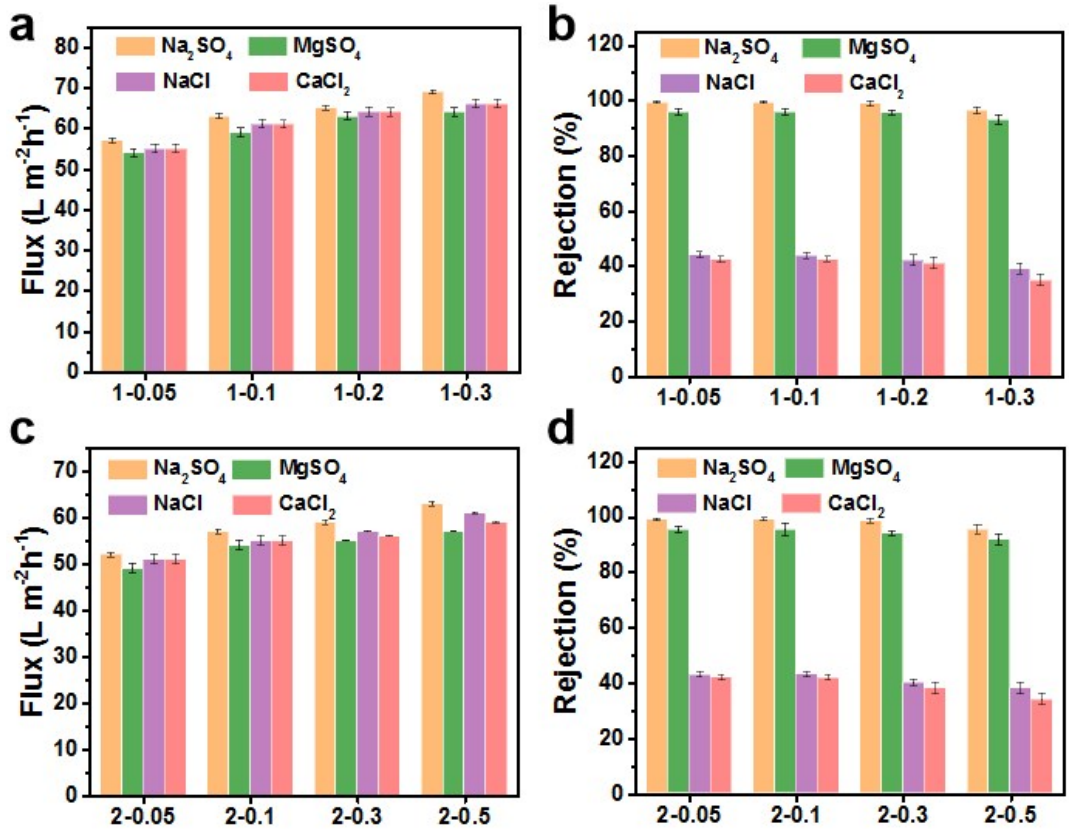

Figure S6 (a, c) Water flux and (b, d) rejection added with different content L-cystine (**1**) and L-cysteine (**2**) for diferent salt aqueous solutions of 2000 ppm at 25 °C and 6 bar.

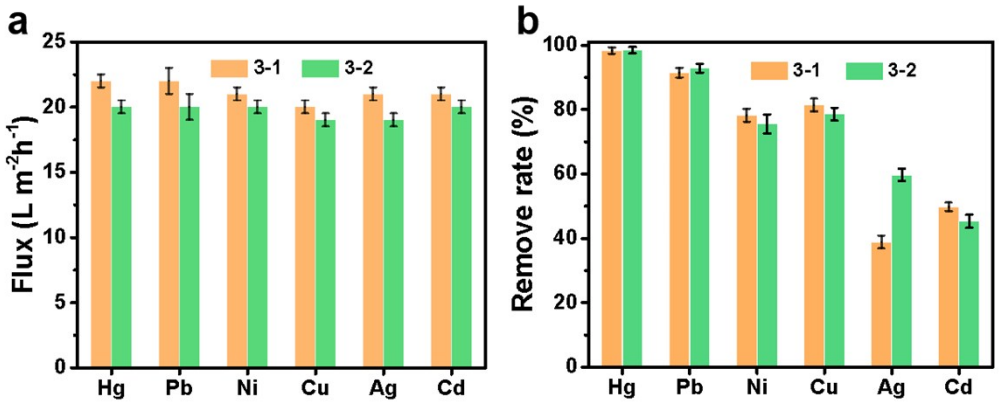

Figure S7 (a)Water flux and (b) remove rate of 3-1 and 3-2 NF active layers for removing heavy metal ions from different aqueous solutions of 10 ppm at 25 °C and 6 bar.

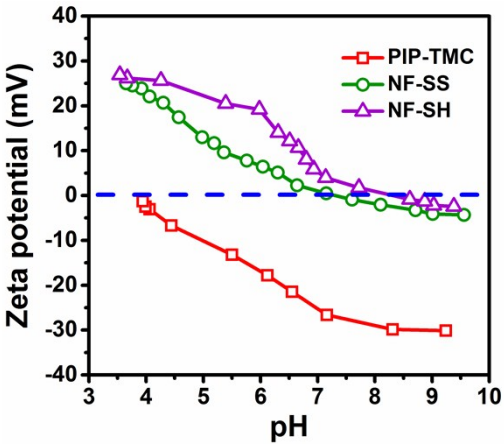

Figure S8 Zeta potentials of PIP-TMC, NF-SS and NF-SH active layers with increasing pH values after 1 h filtration (where the Hg-S complex occurs).

Table S1 Comparison of Hg(II) removal performance of state-of-the-art TFC NF membranes and other benchmark thiol/thio-functionalized porous materials .

Materials	**Mechanism**	**Hg(II) Remove efficiency (%)**	**Final Hg(II) Concentration (ppb)**	**Regeneration**	**Selectivity over Ca(II), Mg(II) , Na(II)**	***Ref.***
NF-SS	Membrane filtration	99.87	1.8	✔	✔	**This work**
NF-SH	Membrane filtration	99.99	0.18	✔	✔	**This work**
a: Modified MOF	Adsorption	84.8	3.05	✘	✘	S1
b: MOF-74-Zn	Adsorption	72.2	13.9	✘	✘	S2
c: TF-SCMNPs	Adsorption	90	169*	✔	N.R	45
d: Zr-DMBD	Adsorption	90*	10	N.R	N.R	S3
e: Cu-based MOF	Adsorption	97.07	19	N.R	N.R	S4

f: CBAP-1(AET)	Adsorption	96	4*	✔	✔	S5
g: S-FMC-900	Adsorption	N. R.	＞10	N.R	N.R	46
h: Mesoporous silica	Adsorption	N. R.	＞4	✔	N.R	S6
i: COF-S-SH	Adsorption	99.94	0.73	✔	✔	38
j: TAPB-BMTTPA-COF	Adsorption	99.9%*	10	✔	✔	39
k: LHMS-1	Ion exchange	～93-98	0.1-17	✔	N.R.	S7
l: PAF-1-SH	Adsorption	99.9	0.4	✔	✔	S8
m: Fe-BTC/PDA	Adsorption	99.8	1.2	✔	✔	40
n: BioMOF	Adsorption	99.95	5	N.R.	✔	S9
o: ZIF-90-SH	Adsorption	96.35	36.5	N.R.	N.R.	S10
p: Hydrogel	Ion exchange	99.9	0.17	✔	✘	S11
q: Cellulose	Membrane filtration	55	121950*	✘	✘	S12

membrane

x indicates it was not achieved under the conditions tested; ✔implies this parameter was tested and showed reasonable performance; N. R. implies that the parameter was not reported and could not be calculated from the presented data; * implies the parameter was calculated from the presented data.

a. Modified MOF, a novel acylamide- and hydroxyl-functionalized MOF material as a high-capacity and collectable adsorbent could remove Hg(II) from acqueous sulutions, especially for ultratrace Hg^{2+} ions in the ppb magnitude.

b. MOF-74-Zn, $Zn_2(DHBDC)(DMF)_2 \cdot (H_2O)_2$ (DHBDC: 2,5-dihydroxy-1,4-benzenedicarboxylic acid) was employed. The MOF adsorbent showed high removal rate of Hg(II) from water, especially for the ultra-low-concentration Hg(II) ions in the ppb magnitude with the removal rate reaching to 54.48%, 69.71%, 72.26% when the initial concentration of Hg(II) is 20 ppb, 40 ppb, 50 ppb, respectively.

c. TF-SCMNPs, a thiol- functionalised silica-coated magnetite nanoparticles.

d. Zr-DMBD is a thiol-laced MOF (where $DMBD_2$-= 2,5-dimercapto-1,4-benzenedicarboxyate).

e. Cu-based MOF, thiol-functionalization of MOFs by choosing a well known three-dimensional (3D) Cu-based MOF, i.e. [Cu_3(BTC)2(H2O)3]n (HKUST-1, BTC = benzene-1,3,5-tricarboxylate)

f. CBAP-1, a highly porous organic polymer was functionalized with either ethylenediamine (EDA) or 2-aminoethanethiol (AET) for Hg^{2+} removal from water mediu. It could efficiently remove >96% of Hg^{2+} ions in 2 min from a 100 ppm of Hg^{2+} solution.

g. S-FMC-900, a sulfur-functionalized mesoporous carbon.

h. Mesoporous silica, a thiol-silica hybrid mesoporous materials. Alkylthiols [tris(methoxy)mercaptopropylsilane, TMMPS] as the functional monolayers were covalently bound to mesoporous supports.

i. COF-S-SH is a covalent organic framework. It can reach 99.94% of the adsorption capacity at equilibrium within 10 min, and was able to decrease Hg^{2+} concentration from 5 ppm to 0.73 ppb within 30 min of contact in the presence of a very small amount of adsorbent (V/m at 46500 mL g^{-1}). Prolonging the contact time to 3 h, the Hg^{2+} concentration was diminished below 0.1 ppb for Hg.

j. TAPB-BMTTPA-COF, to prepare the hexagonal TAPB-BMTTPA-COF, 1,3,5-tris(4-aminophenyl)benzene (TAPB) was used as a knot and 2,5- bis(methylthio)terephthalaldehyde (BMTTPA) as linker. We observed extremely quick removal process, whereas over 99% of Hg(II)

ions was removed within 5 min. The purification process completes within 15 min and reduced the Hg(II) ions concentration from 10 ppm to 10 ppb.

k. LHMS-1 is a layered hydrogen metal sulfide with the chemical formula H2xMnxSn3-xS6 (x ¼ 0.11-0.25). It should be noted that while the material works in 2 minutes, it is only tested in 67 ppb solutions. To enhance the amount of Hg absorbed, the longer contact time of LHMS-1/water is need.

l. PAF-1-SH, also referred to as the mercury nanotrap, is a porous organic polymer. The resultant materials can efficiently remove 99.9% mercury and decrease the Hg(II) concentration in the solution to 0.4 ppb, but after 6h.

m. Fe-BTC/PDA, meta-organic framework/polymer composite.

n. BioMOF, a MOF with the formula $CaCu_6[(S,S)\text{-methox}]_3(OH)_2(H_2O)\} \cdot 16H_2O$ that is decorated with thioalkyl chains.

o. ZIF-90-SH, a thiol-functionalized ZIF-90 with zeolitic imidazolate structure (ZIF-90-SH) employed as an adsorbent was effective in the treatment of low-concentrations of Hg (II) (10.0-0.1 mg L^{-1}) resulting in 96-98% removal of Hg (II) from aqueous solution.

p. Hydrogel, a novel hydrogel, immobilized of two polyelectrolytes, was able to reduce the concentration of Hg(II) from 200 and 500 ppb to 0.20 and 0.17 ppb, respectively, after 30 min.

q. Cellulose membrane is a diaminobutane based poly(propyleneimine) dendrimer functionalized with sixteen thiol groups, DAB-3-(SH)16, was successfully embeded in a swollen cellulosic support in order to achieve an easily handle engineered membrane for heavy metals removal.

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