Electronic Supporting Information

Ultra-high permeability membrane composed of graphene oxide nanosheets supported by MOF framework utilized for dye separation

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Experimental Section

Materials.

Graphite powder, concentrated sulfuric acid (H_2SO_4, 98%), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30%), 2-amino-terephthalic acid, methanol and Congo red (CR), the raw materials were purchased from Shanghai Aladdin Biochemical Technology Co., LTD. Zirconium chloride ($ZrCl_4$, 99.5%) was purchased from Shanghai Maclin Biochemical Co., LTD. N,N-dimethylformamide (DMF) was purchased from Chengdu Colon Chemical Co., LTD. UN100 ultrafiltration membrane (UN100 UF) was used as the base membrane in the experiment. The base membrane was purchased from Shanghai Huamao Industrial Co.,LTD via Taobao. Deionised water (resistivity >18.2MΩ·cm-1) is produced by an ultrapure water machine purchased from Sichuan Youpu Ultra-Pure Technology Co., LTD.

Synthesis of GO and UiO-66-NH$_2$.

Graphene oxide was synthesized using modified Hummer's method[1]. Firstly, the concentrated sulfuric acid (H_2SO_4, 98%, 50 mL) was slowly added in a flask which contained graphite powers (2.0 g). The mixed solution was stirred in an ice bath for 1 h. Secondly, potassium permanganate ($KMnO_4$, 6 g) was slowly added and vigorously stirred for 30 min at <10 °C. Thirdly, the mixed solution was heated to 35 °C for 30 min and then, distilled water (90 mL) was slowly added under stirring (15 min). Then, the temperature was elevated to 98 °C for 30 min, and hydrogen peroxide (H_2O_2, 30%, 20 mL) was added. Finally, the graphite oxide was harvested after being washed with deionized water and dried.

UiO-66-NH$_2$ was synthesized via the solvothermal method[2]. The UiO-66-NH$_2$ nanoparticles were synthesized by dissolving 650 mg $ZrCl_4$, 480 mg 2-aminoterephthalic acid and 7.56 g deionized water in 160 mL N,N-dimethylformamide (DMF). Then the DMF solution was

sonicated using a ultrasonic cell crusher for 5 min to produce a homogeneous solution. Afterwards, the solution was heated at 150 °C for 24 h. After centrifugation at 10,000 rpm for 10 min, the sediments were collected and washed by methanol for 3 times firstly, then washed by water for 5 times. Finally, the UiO-66-NH$_2$ nanoparticles were obtained.

Preparation of GO and UiO/GO membranes.

Firstly, 0.5 mg of GO powder was added to 500 ml of deionised water to make a 0.001 mg/ml dispersion. Secondly, 5 mg of UiO-66-NH$_2$ powder was added to 500 ml of deionised water to prepare 0.01 mg/ml dispersion solution. After ultrasonic dispersion and magnetic stirring for 30 min, a uniform dispersion solution was obtained. The dispersion liquid of 10 ml, 7 ml, 5 ml, 3 ml and 1 ml of GO was uniformly loaded onto the surface of UN100 UF through a vacuum filtration device (effective diameter 40 mm), and the resulting membranes were named GOM-1, GOM-2, GOM-3, GOM-4 and GOM-5.

Take 5ml of GO dispersion solution and add different amounts of 0.1 ml, 0.3 ml, 0.5 ml, 1 ml and 1.5 ml of UiO-66-NH$_2$ dispersion solution respectively. Ultrasonic dispersion for 30 min. Finally, the UiO/GO dispersion was also uniformly pumped into the membrane ultrafiltration membrane through the vacuum filtration device, and the resulting membranes were named M1, M2, M3, M4 and M5. At the same time, the GOM-3 was designated M-0 to compare the change in performance.

Preparation of dye solution.

In order to study the separation performance of the composite membrane, 100 ppm CR solution was prepared. Add 100 mg CR dye to 1.0 L deionized water and stir magnetically for 30 min to obtain 100 ppm CR solution.

Membrane performance evaluation system.

Membrane performance evaluation: Evaluation of membrane performance using a cross-flow filtration system. The membrane separation device was purchased from Hangzhou Saifei Membrane Separation Technology Co., LTD. The effective membrane area is 7.0 cm^2, the feed flow rate is 30.0 L h^{-1}, and the applied pressure is 2.0 bar. The test process is to compacted three membranes with the same preparation conditions into three membrane pools. The pure water is prepressed for 40 min, and the stable water permeability is calculated by the change of the quality of the liquid. Replace it with 100 ppm CR solution for 30 min for pre-pressing, in which the internal circulation between the liquid and the mother liquid is carried out in order to prevent concentration polarization. The water permeability was then measured and the permeant and mother liquor were preserved. The water permeability is calculated by the continuous output of data quality changes from the OHAUS weighing station to the computer. Ultraviolet visible spectrophotometer (UV5200PC, Shanghai Yuan Analysis Instrument Co., LTD.) was used to determine the concentration of dye in the solution. The removal rate of dye is calculated by equation (1) :

$$R = \left(1 - \frac{C_1}{C_0}\right) \times 100\%$$

(1)

Characterization.

The emission scanning electron microscope (FESEM, Sigma 500) was equipped with energy dispersive spectrometer (EDS) to characterize the micromorphology and element distribution of the samples. SEM images were obtained using InLens secondary electron detector with an acceleration voltage of 15 KV, and an aperture size of 60 μm. Surface roughness of different samples was analyzed by atomic force microscopy (AFM) (Dimension EDGE, Bruker). The

crystal structure of the sample was detected by X-ray Diffractometer (XRD, D8 Advance), where the XRD target was copper and the wavelength of the X-ray was 0.154056 nm, the Angle range was 5°−80°, and the step size was 0.02°. The specific surface area and pore volume of the samples were measured using a nitrogen adsorption desorption system (MIC-2460) through the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. All the samples were degassed at 200℃ for 6 hours prior to the measurements. In attenuated total reflection (ATR) mode, Fourier Transform infrared Spectrometer (FTIR Spectrometer, Nicolet iS50) was used to analyze the group type and molecular structure of the material. The elemental and chemical valence states of the samples were characterized by X-ray photoelectron spectroscopy (XPS, Escalab 250XI). XPS has an energy resolution of 0.45 eV, a step size of 1 eV, a CAE pass energy of 100 eV, a working voltage of 14.6 KV, and a working current of 10 mA. The electron binding energy of the spectrum was calibrated, and the peak of C1s was 284.8 eV.

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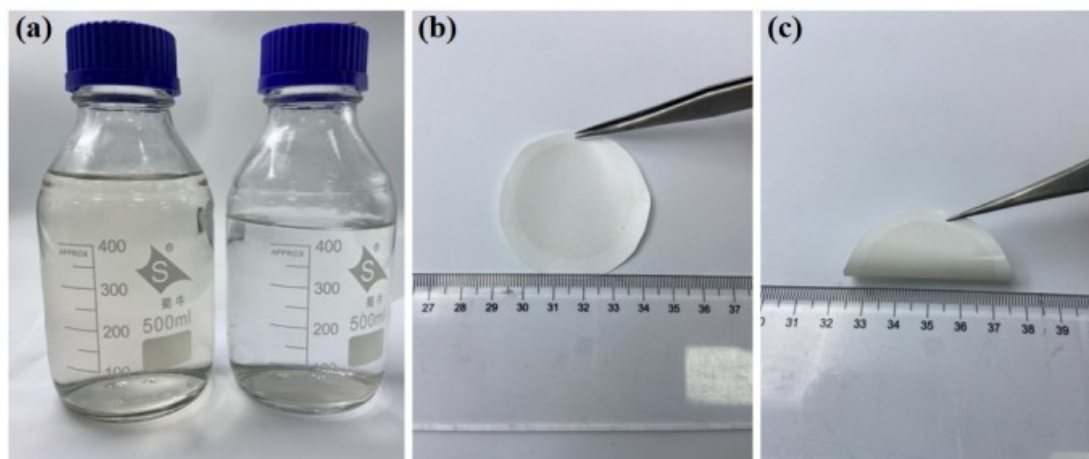
Supplementary Figures

Fig. S1 (a) Photograph of GO and UiO-66-NH$_2$ dispersion (GO dispersion concentration 0.001mg/ml, UiO-66-NH$_2$ dispersion concentration 0.01mg/ml), (b) A photograph of the GOM-3 and (c) A photograph of the M4.
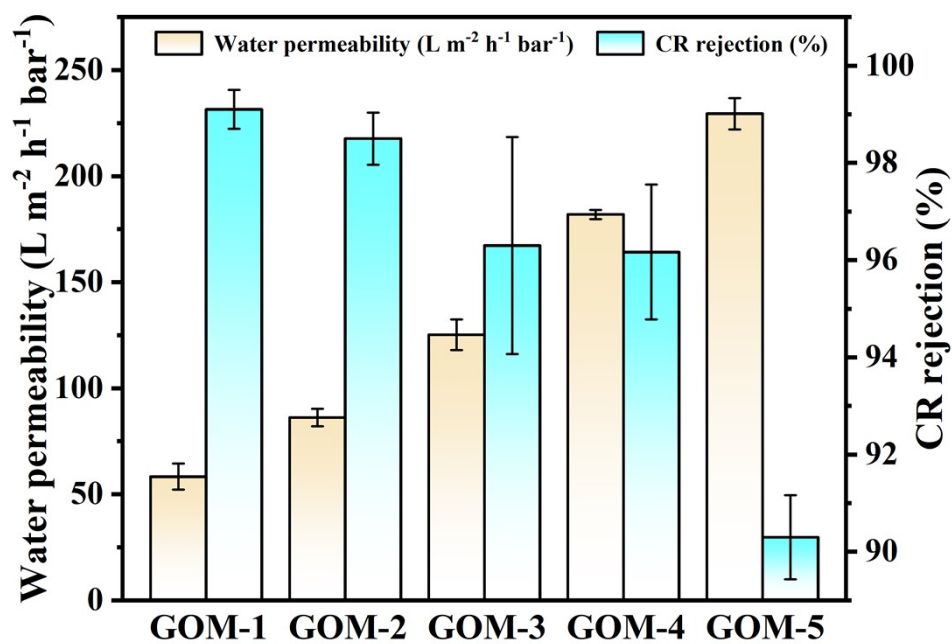

Fig. S2 Pure water permeability and CR rejection rate of GO membranes with different concentrations.

Fig. S3 (a-b) Top view and main view of cross-flow filtration apparatus, (c) Mother liquid and permeate liquid before and after separation of the M4 membrane.
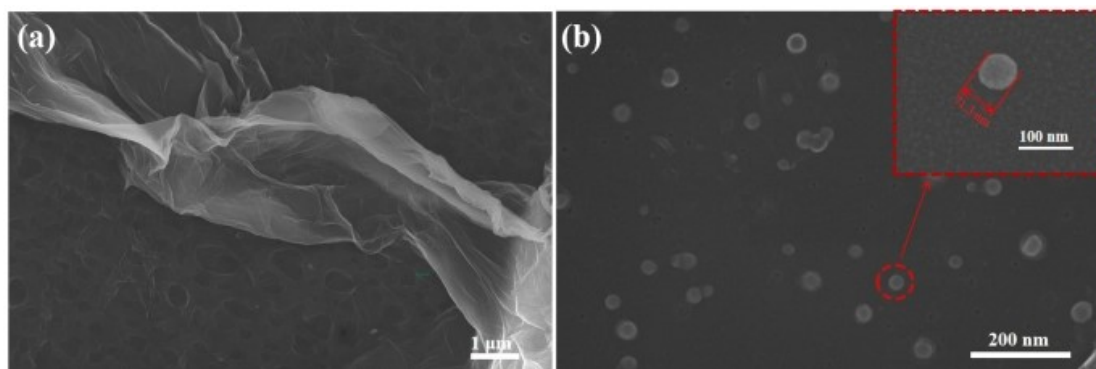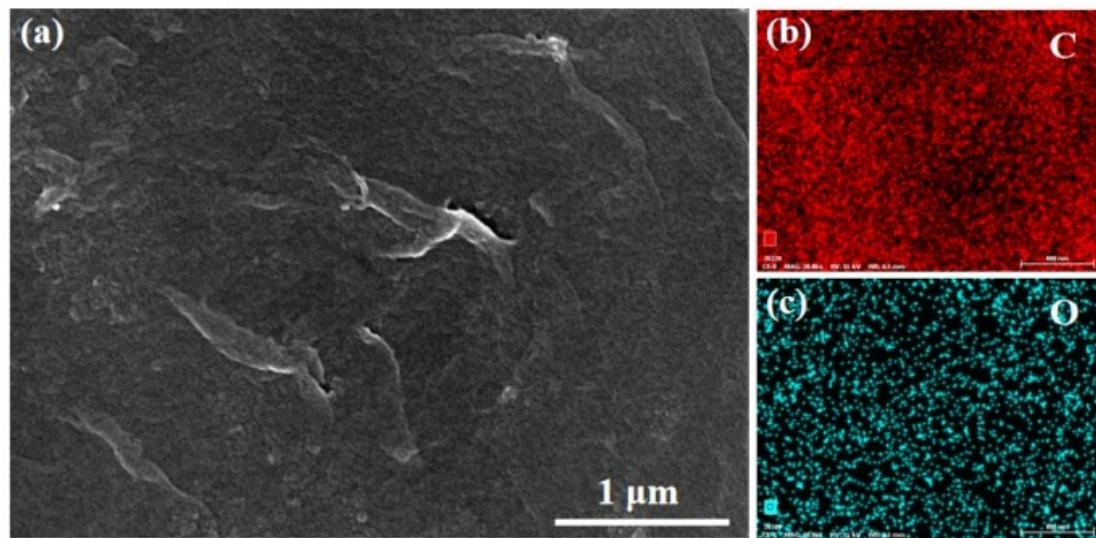

Fig. S4 FESEM images of GO (a) and UiO-66-NH$_2$ (b).

Fig. S5 FESEM image and EDS spectrum of GO membrane.
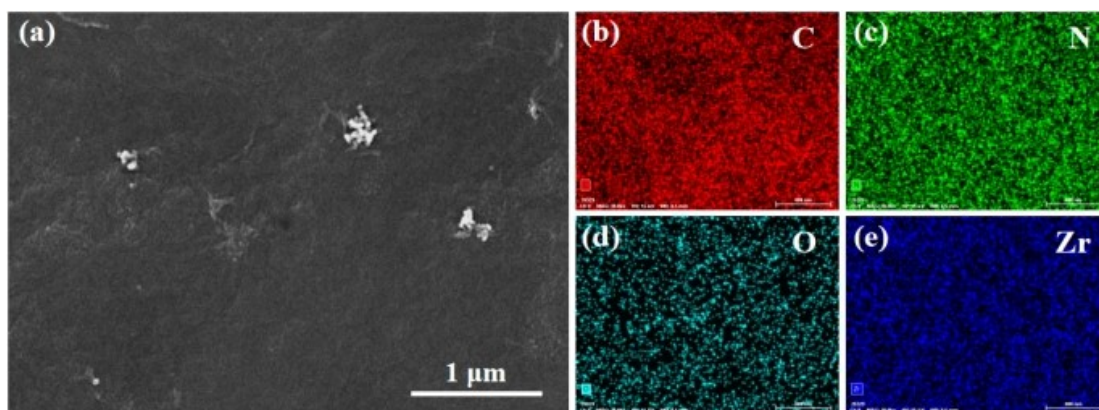
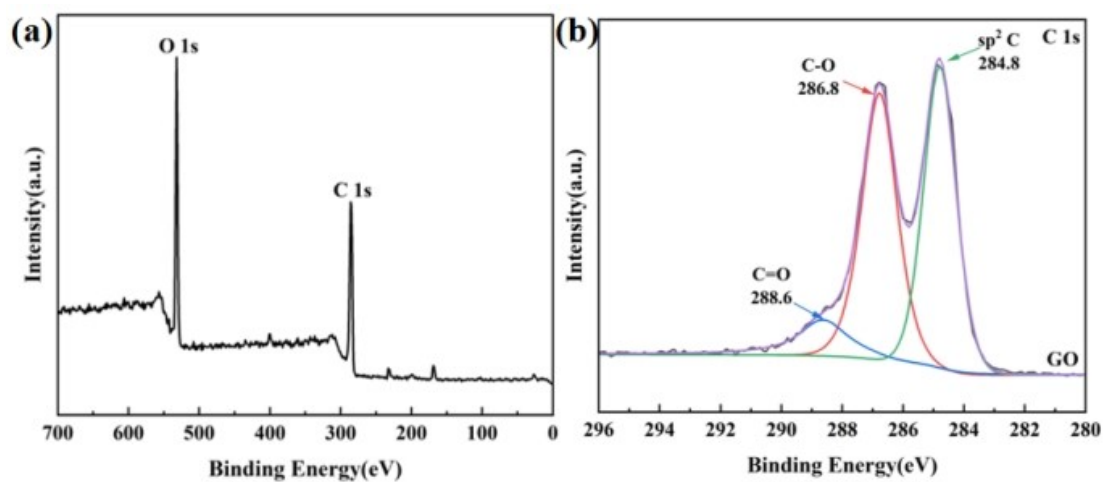**Fig. S6** FESEM image and EDS spectrum of UiO/GO membrane.

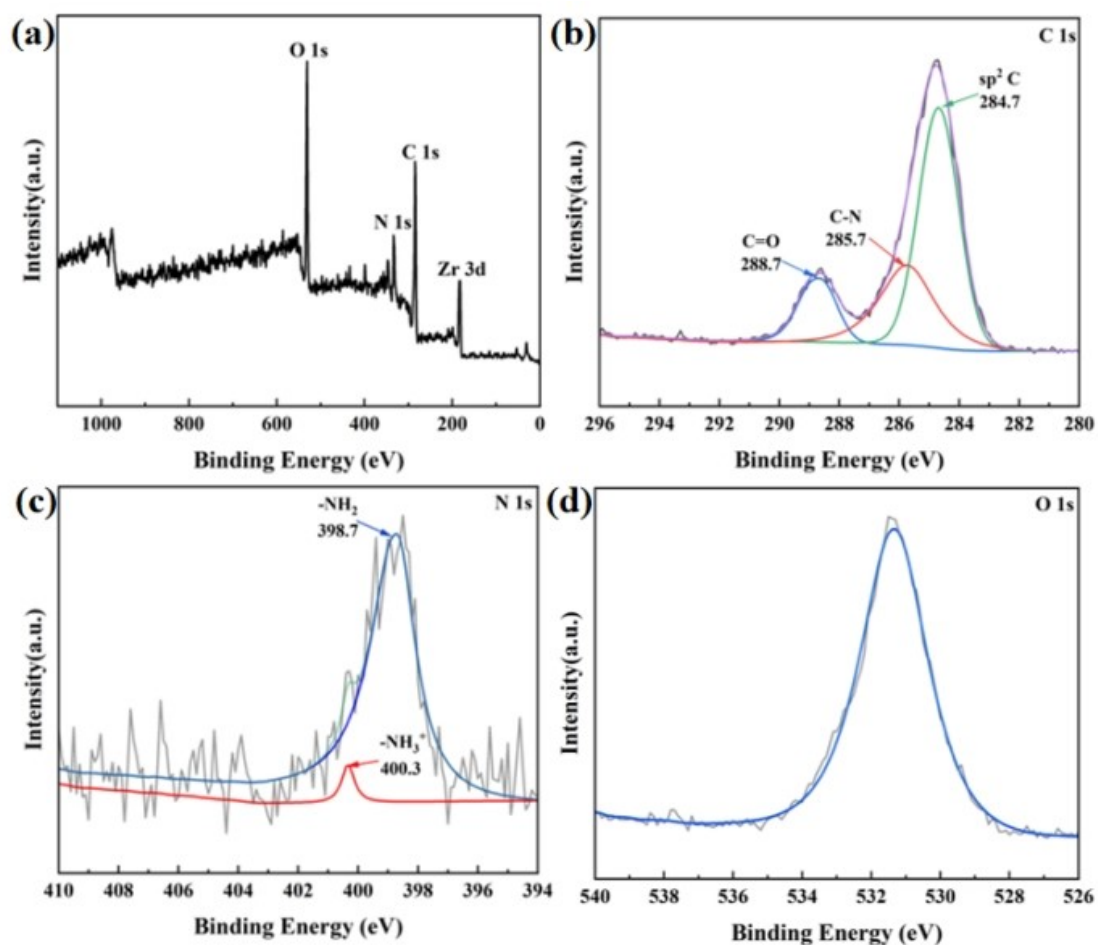**Fig. S7** (a) XPS spectrum of GO and (b) XPS C 1s spectrum of GO.

Fig. S8 (a) XPS spectrum of UiO-66-NH$_2$, (b) XPS C 1s spectrum, (c) XPS N 1s spectrum and (d) XPS O 1s spectrum of UiO-66-NH$_2$
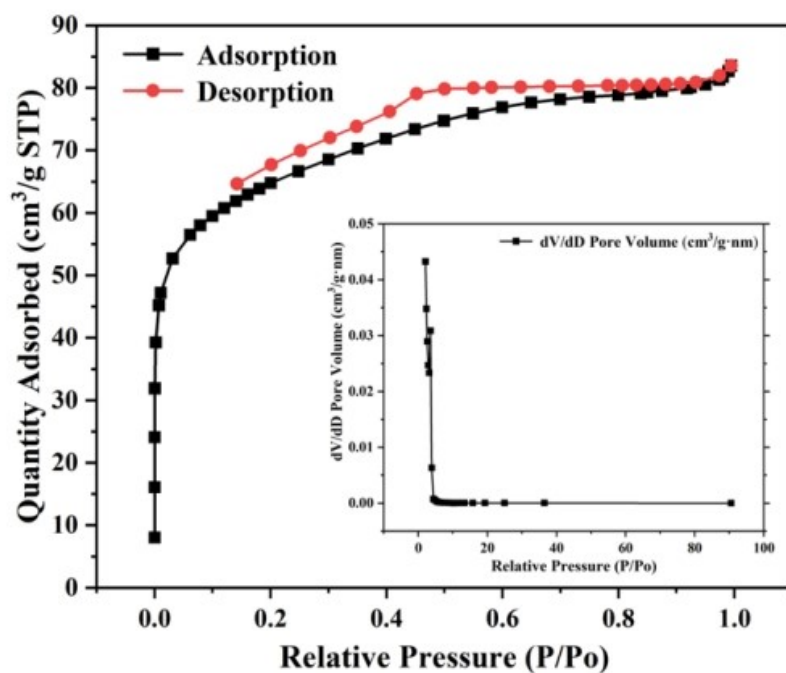

Fig. S9 The specific surface area and pore volume of UiO-66-NH$_2$ determined by the BET and BJH approach from the desorption branches of N2 adsorption-desorption isotherms.

Supplementary Table

Table S1 Comparison with similar state-of-the-art MOF/GO membranes in the literature

Membrane	Preparation method	Basement membrane	Testing conditions	Permeate flux (L m^{-2} h^{-1} bar^{-1})	Separated substance	Feed concentration (ppm)	Rejection rate (%)	Ref.
GO@PTCDA-UiO-66-NH$_2$	Vacuum filtration	The mixed cellulose (MCE, 0.22 μm)	Dead-end fifiltration, 1bar	83.5	MB, CR	100	99.9, 99.9	1
GO@Al-MOF	Vacuum filtration	Anodized aluminum oxide membrane (AAO, 100 nm)	Dead-end fifiltration, 1bar	51.6	CR	100	99.9	2
UiO-66@GO-CS	Pressure-assisted self-assembly filtration	Polyvinylidene fluoride (PVDF)	Permeation module, 3bar	14.2	MO, MnB	200	99.0, 97.0	3
ZIF-8@f-GOm	Vacuum filtration	alumina tube membrane	Cross-flow filtration, 1 bar	60.0	MB	100	~100	4
eZIF-8/GO	Vacuum filtration	Polysulfone (PSF)	Cross-flow filtration, 2 bar	45.4	CR	50	99.0	5
CuTz-1/GO	Vacuum filtration	Hydrolyzed PAN (HPAN)	Cross-flow filtration, 4 bar	40.2	CR, Direct red, MB	500	99.4, 98.2, 94.9	6
Cu-TCPP/GO	Vacuum filtration	Polyethersulfone (PES)	Cross-flow filtration, 2 bar	26.2	CR	20	96.7	7
Zn-TCPP/rGO	Vacuum filtration	Nylon (0.2 μm)	Cross-flow filtration, 4 bar	19.0	MB, MnB	50	99.0, 37.4	8
UiO/GO	Vacuum filtration	UN100 UF	Cross-flow filtration, 2 bar	136.4	CR	100	98.2	This work

[a] CR: congo red; MB: methyl blue; MnB: methylene blue; MO: methyl orange

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