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Clay adsorptive membranes for chromium removal from water

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Abstract. Cost effective clay adsorptive microfiltration membranes were synthesized to remove Cr (III) from high polluted water. Raw and calcined bentonite were mixed in order to decrease the shrinkage and also increase the porosity; then, 20 wt% of carbonate was added and the samples, named B (without carbonate) and B-Ca20 (with 20 wt% calcium carbonate) were uniaxially pressed and after sufficient drying, fired at 1100°C for 3 hours. Then, physical and mechanical properties of the samples, their phase analyses and microstructure and also their ability for Cr(III) removal from high polluted water (including 1000 ppm Cr (III) ions) were studied. Results showed that the addition of calcium carbonate lead the porosity to increase to 33.5% while contrary to organic pore formers like starch, due to the formation of wollastonite, the mechanical strength not only didn't collapse but also improved to 36.77 MPa. Besides, sample B-Ca20, due to the presence of wollastonite and anorthite, could remove 99.97% of Cr (III) ions. Hence, a very economic and cost effective combination of membrane filtration and adsorption technology was achieved for water treatment which made microfiltration membranes act even better than nanofiltration ones without using any adsorptive nano particles.

Keywords: water treatment, Cr(III) removal, clay adsorptive membrane, microfiltration, wollastonite, anorthite, cost effective

1. Introduction

Heavy metal ions (i.e., Cr, Ni, Pb, …) can be absorbed and accumulated in human bodies and cause serious diseases like nervous system problems, cancers and in extreme cases, death (Gunatilake 2015). Chromium is one of the most hazardous inorganic water pollutants which is constantly released into water resources by natural (mainly by volcanic activity and weathering of rocks) and industrial (mainly leather industry) processes (Kocurek *et al*. 2014 and Mousavi Rad *et al*. 2009). Cr (VI) is considered as the harmful and toxic form of chromium and is carcinogen. Cr (III) is less toxic than Cr (VI) but when it is released to the environment, at high concentrations of oxygen or in contact with manganese dioxide (MnO_2) it oxides to Cr (VI) (Jacobs and Testa 2004, Shadreck and Mugadza 2013). Pressure-driven membrane separation processes (nanofiltration and reverse osmosis) and adsorption mechanisms are two ways used for heavy metal removal (Mousavi Rad *et al*. 2009). Membrane processes are widely used in water treatment since access to drinkable water has become one of the challenges of this century. In the environmental field, since great volumes of water and wastewater are generally treated, great surface areas of membranes are needed. Using low cost ceramic membranes such as clays seems to be an efficient solution to treat wastewater (Belibi Belibi *et al*. 2015). Addition of alkaline-earth carbonates (calcite and dolomite) to clay membranes would increase their porosity, while due to a decrease in the sintering temperature as a result of low temperature melting and strengthening phases formation such as wollastonite, despite organic pore formers, not only won't decrease the membrane's strength, but also will increase it (Lorente-Ayza *et al*. 2015 and Endo *et al*. 1994).

Combination of membrane filtration process with other separation mechanisms such as adsorption, in hybrid systems, has developed recently. Hybrid adsorption/membrane separation, i.e., using a membrane filtration together with adsorptive nano particles, was found as an effective method to enhance adsorption capacity and the quality of treated water (Hammami *et al*. 2017, El-Gendi *et al. 2016* and Zhang *et al. 2016*). Hybrid membrane process is being increasingly used to improve the efficiency of water treatment systems. In these systems, adsorption part can be prior to filtration part, post to it or integrated with filtration section (Stoquarta *et al*. 2012).

Adsorptive membranes, i.e., membranes which can adsorb impurities without using any extra adsorptive particles, are somehow similar to the integrated hybrid systems, as they both simultaneously treat water by adsorption and membrane filtration, but in the integrated hybrid system, maintaining the system is not easy and needs aeration to avoid membrane fouling (Stoquarta *et al*. 2012) while adsorptive membranes don't use any adsorptive particles to cause that problem. Using adsorptive membranes is a new and developing method for water treatment which can be considered as a combination of adsorption and membrane technology. In these kinds of membranes, membrane is an obstacle between the effluent and permeate and adsorption is the selective mechanism

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(Hoff K. A. 2003).

Clay membranes, due to the formation of alkaline-earth aluminosilicates and pyroxenes, such as anorthite and wollastonite during their firing procedure, can adsorb heavy metal ions from water effectively (Xirokostas *et al.* 2003, Zhao *et al.* 2017, Ziegler F. 2000, Babel and Kurniawan 2003, Bhatnagar and Minocha 2006 and Panday *et al.* 1986).

In this research, clay adsorptive microfiltration membranes were synthesized from inexpensive raw materials (local bentonite and calcium carbonate). Physical and mechanical properties were studied and also phase and microstructure studies were done to verify whether the synthesized membranes were suitable for water treatment according to the literature. Then their chromium (III) ions removal from water was studied.

2. Material and methods

2.1 Materials

Chemical analyses of the starting materials used in this work are listed in Table 1. In order to create Cr (III) ions to make polluted water, $Cr(NO_3)_3.9H_2O$ (Merck 102481) was used.

2.2 Membrane preparation

In the previous researches of these authors, in order to decrease the shrinkage and also increase the porosity of clay membranes, different percentages of raw and calcined bentonite were mixed and their physical and mechanical properties were compared and 33% of calcined bentonite was chosen as the best composition. Then, according to other researchers, 20% of calcium carbonate, 20% of magnesium carbonate and 20% of their mixture were added to bentonite (including 33% calcined and the rest raw bentonite). These samples were fired and their properties were evaluated and found that 20% of calcium carbonate lead to the best results. In this research, calcium carbonate containing samples are compared with without carbonate ones in different characteristics.

Two compositions were prepared according to Table 2. In order to decrease the shrinkage and also increase the porosity, 33% of bentonite in each sample was calcined at 1000°C before mixing. Calcium carbonate was used as a pore former besides increasing the mechanical strength through forming low temperature melting phases and increasing the Cr (III) adsorption by formation of aluminosilicates and pyroxenes.

Table 1 Chemical analyses of the starting materials

	SiO₂ (wt%)	Al₂O₃ (wt%)	Fe₂O₃ (wt%)	MgO (wt%)	CaO (wt%)	K₂O (wt%)	L.O.I.[*] (wt%)
Bentonite	67.8	11.7	0.9	2.3	4	1.1	11.9
Calcium Carbonate	-	-	0.4	1.3	54.9	-	43.11

[*]Loss on ignition

Table 2 Compositions of the samples

	Bentonite (wt%)	CaCO₃ (wt%)
B	100	0
B-Ca20	80	20

After wet-mixing for 1 hour, the mixture slurry was dried for 24 hours at 110°C. Afterwards, the mixture was passed through 200 mesh sieve. The requisite amount was then mixed with 5 wt% of PVA solution (5% wt in 100ml distilled water), as an organic binder, and then uniaxially pressed at the pressure of 500 psi. The disc shape prepared membranes (35 mm diameter and 8 mm thick) were then dried at 110∘C for 24 h. Then the membranes were fired in an electrical furnace at 1100°C for 3 hours with the rate of 2°C/min.

2.3 Characterization techniques

2.3.1 Physical and mechanical properties

The firing shrinkage was calculated for each sample, using the diameters of dried and fired samples. Bulk density and apparent porosity of the samples were evaluated by Archimedes' principle. Mechanical strength (M.O.R)[*] of each sample was examined according to Eq.1, where P is the fracture load (N), L is the distance between the levers (mm), b is the width and d is the thickness of the samples (mm).

$$M.O.R\ (MPa) = (3PL)/(2bd^2) \tag{1}$$

2.3.2 Phase analyses and microstructure

Phase analyses of raw bentonite and the samples were studied through X-ray diffraction (PANalytical, Cu K*a*, 40kV). A comparison between the results of quantitative phase analyses derived from chemical analyses and the results of Rietveld method show a satisfactory agreement according to Ufer *et al.* (2008) though the approximate amounts of the phases were calculated with regarding to the chemical analyses of the starting materials (Table 1) and the compositions of the samples (Table 2).

The surface morphologies were investigated using scanning electron microscope (Vega II Tescan) and the approximate pore size distribution were derived from the SEM micrographs using ImageJ software.

2.3.3 Filtration test

In order to evaluate the ability of Cr (III) removal by each sample, two different types of feed solution (one, 5 ppm Cr (III) ions in deionized water (within the drinking water range) and another one 1000ppm Cr(III) ions in deionized water (within tannery effluent range) were tested.

A home-made dead-end set up (Fig. 1) was used in which the feed solution is passed through the membrane modulus with the aid of an HPLC pump (Flow rate= 3 and 8 lit/min) (in the case of 5 ppm) and a little aquarium pump (Nominal Flow rate=5 lit/min) (in the case of 1000 ppm)
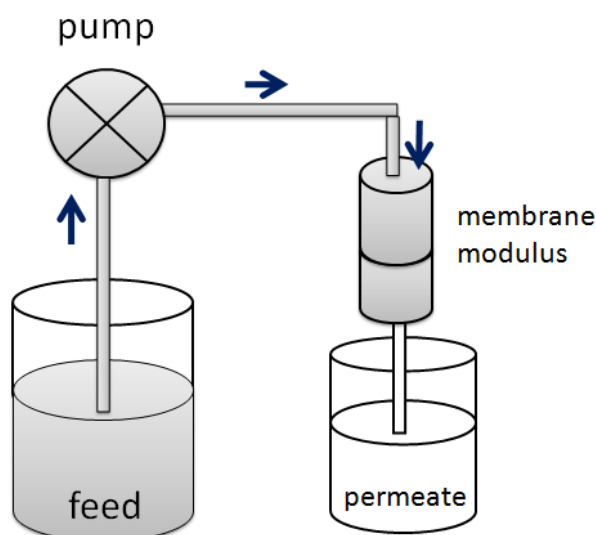
[*]Modulus of rupture

Fig. 1 Schematic view of the filtration system

Table 3 Physical and mechanical properties of the samples

	Firing shrinkage (%)	Apparent porosity (%)	Bulk density (g/cm3)	M.O.R (MPa)
B	3.57	26.4	1.77	26.1
B-Ca20	2.31	33.5	1.64	36.77

and then the filtrate from each sample was examined by Atomic Absorption (Shimadzu-AA 6300).

Different flow rates were tested to study the effect of time on Cr (III) ions removal, as the effective mechanism of removal is adsorption and it is a time dependent mechanism.

3. Results and discussion

3.1 Physical and mechanical properties

Physical and mechanical properties of the samples are given in Table 3. The given results are the mean of at least 2 results.

In Table 3, it can be seen that the addition of calcium carbonate leads the shrinkage of clay membranes to decrease from 3.57 to 2.31% due to the reaction between CaO and other constituents and formation of calcium aluminosilicates (Claudia Lira *et al*. 1998). Firing shrinkages below 2.7% are said to be desirable for clay membranes according to Vasanth *et al*. (2011).

Table 3 also shows that by addition of calcium carbonate, the porosity of clay membranes improves and so the bulk density decreases from 1.77 to 1.64 g/cm^3 which is desirable for clay membranes according to Eom *et al*. (2015), Mohamed Bazin *et al*. (2014) and Lee *et al*. (2015). It is also seen that the addition of calcium carbonate, due to the CO_2 release, leads the apparent porosity to increase from 26.4% to 33.5%, which is appropriate for clay membranes according to Lorente-Ayza *et al*. (2015) and Vasanth *et al*. (2011).

The effect of calcium carbonate addition on the flexural strength of clay membranes can be also seen in Table 3. It
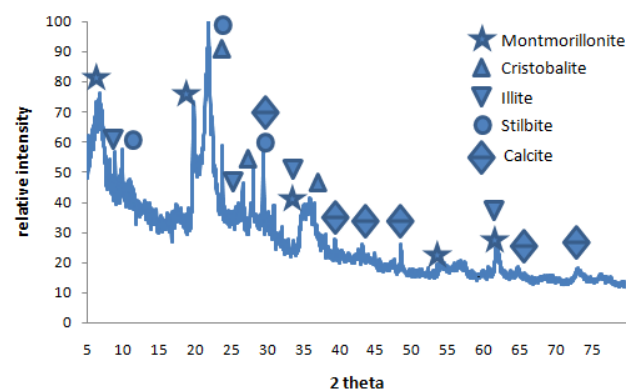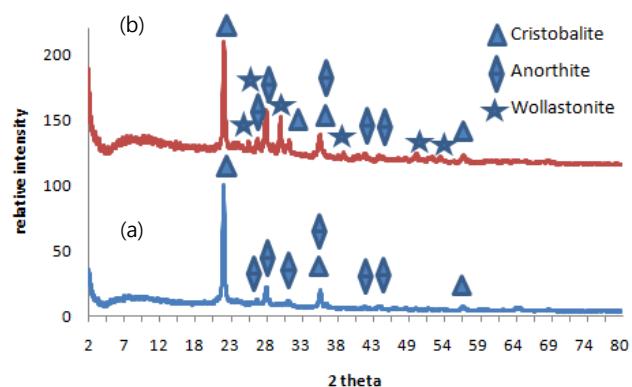

Fig. 2 The XRD pattern of raw bentonite

Fig. 3 The XRD pattern of the samples: (a) B and (b) B-Ca20

can be seen that calcium carbonate addition improves the flexural strength from 26.1 MPa to 36.77 MPa which can be attributed to the formation of wollastonite (Endo *et al*. 1994). Wollastonite increases the fracture toughness and thermal shock and so strengthens the ceramic bodies (Endo *et al*. 1994 and Svab *et al*. 2009). The flexural strength of clay-based membranes has been reported between 18-34 MPa by other researchers according to Eom *et al*. (2015).

3.2 Phase studies

Figs. 2 and 3 show the XRD patterns of raw bentonite and the fired samples, respectively. Fig. 2 shows that montmorillonite, cristobalite, illte, stilbite and calcite are detected in bentonite which is corroborated with clay analyses (Karnland *et al*. 2006) and the approximate amounts of the phases (Ufer *et al*. 2008), are around 46%, 25%, 9%, 8% and 6%, respectively.

The presence of anorthite or calcic feldspar is expected in aluminosilicate systems including CaO at temperatures around 900°C (Vasanth *et al*. 2011 and Monash and Pugazhenthi 2011). It can be seen that cristobalite (SiO_2) and anorthite ($CaAl_2Si2O_8$) are detected in sample B (Fig. 3-a) and the approximate amount of each phase, calculated with regarding to the starting materials' chemical analyses (Table 1) and the composition of the samples (Ufer *et al*. 2008) is shown in Table 4.
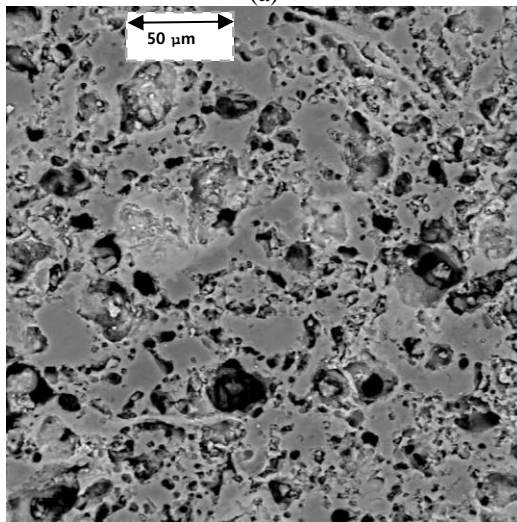
According to Fig. 3-b, cristobalite, anorthite and wollastonite ($CaSiO_3$) are detected in sample B-Ca20.

Table 4 Semi-quantitative phase analyses of the samples

|	Cristobalite(wt%)	Anorthite(wt%)	Wollastonite(wt%)
B	67	23	-
B-Ca20	42	31	22
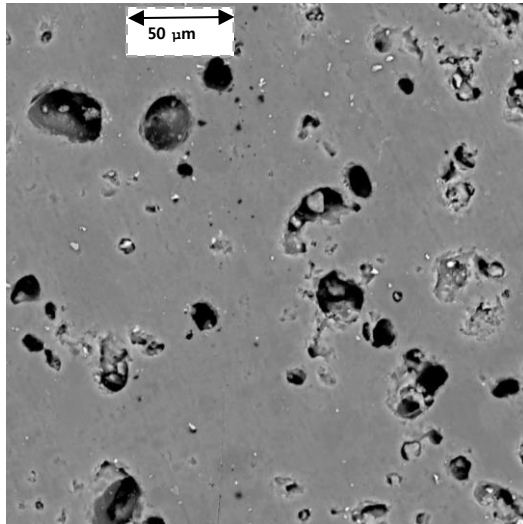
(a)

(b)

Fig. 4 Polished surfaces of the samples: (a) B (b) B-Ca20

Anorthite and wollastonite are the expected crystalline phases when a mixture of clay and calcium carbonate is sintered at around 1100°C. The amount of calcium silicate (wollastonite) and calcium aluminosilicate (anorthite) phases mainly depends on the relative amount of aluminium, calcium and silicon oxides present in the starting composition (Vasanth *et al.* 2011, Monash and Pugazhenthi 2011, Huang *et al.* 1994 and Ghouil *et al.* 2016). The approximate amounts of each phase, calculated with considering to chemical analyses (Table 1) and the composition of the samples (Table 2) (Ufer *et al.* 2008) is shown in Table 4. Wollastonite shows high values of bending strength and Vickers hardness when sintered at about 1100°C which is expected to be closely related to the formation and consolidation of platy particles with size uniformity in the sintered body (Endo *et al.* 1994).
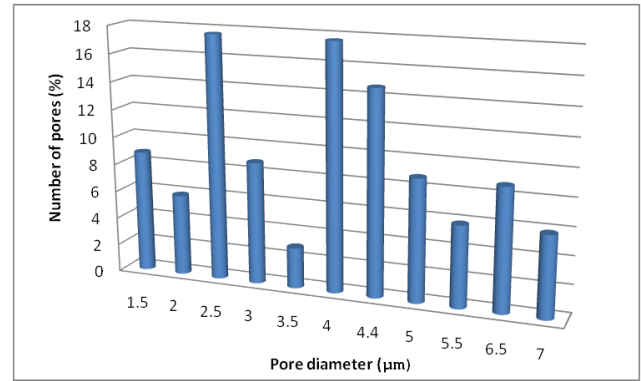
(a)
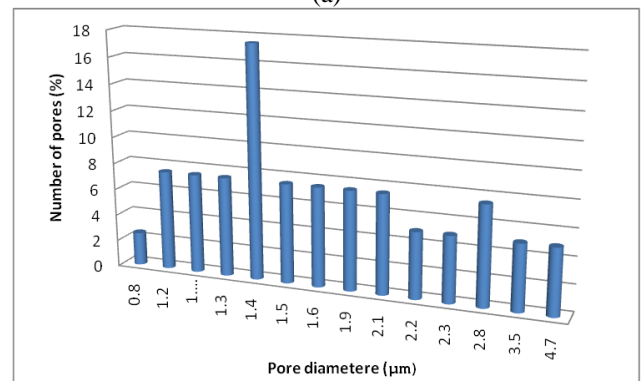
(b)

Fig. 5 Pore size distribution of the samples fired at 1100°C for 3 hours: (a) B (b) B-Ca20

3.3 Microstructure studies

The microstructures of the polished surfaces of the samples are shown in Fig. 4. It can be seen that by addition of calcium carbonate, a porous surface is obtained and the pores are well distributed on the surface of the sample.

Addition of calcite to the ceramic bodies leads to formation of porous structures while decreases the sintering temperature which strengthens the body (German *et al.* 2008). Large pores in sample B-Ca20 can be due to the accumulation of $CaCO_3$ powder in the composition and its decomposition during firing process (Eom *et al.* 2015).

3.4 Pore size distribution and mean pore size

The pore size distributions of the samples and their mean pore sizes are derived from the SEM images and measured by ImageJ software (Vasanth *et al.* 2011, Monash and Pugazhenthi 2011) (Fig. 5).

It can be seen that the mean pore sizes in sample B (Fig. 5-a) are around 2.35 and 3.75 µm and the mean pore size is unified and decreased to around 1.45 µm by addition of calcium carbonate in sample B-Ca20 (Fig. 5-b), which is attributed due to the formation of liquid phases (German *et al.* 2008). It can be also seen that the pore size distribution in sample B-Ca20 (Fig. 5-b) has more uniformity than sample B. Membranes with mean pore sizes in the range of 0.1- 10 µm are classified as microfiltration membranes (Strathmann 2011) and 1.4 µm is reported as an acceptable mean pore size for clay membranes according to Vasanth *et al.* (2011).
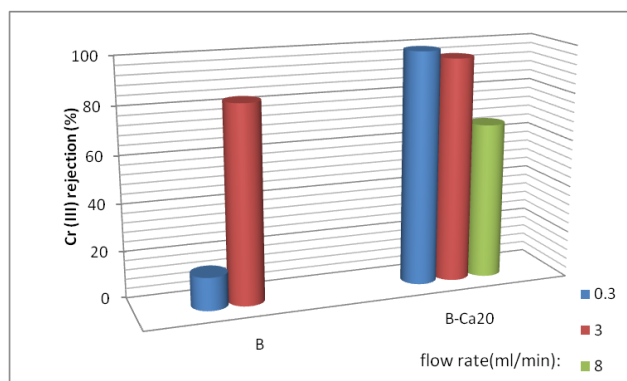
Fig. 6 Effect of calcium carbonate addition and flow rate on Cr (III) ions rejection. Concentration of feed solution at flow rate 0.3 ml/min: 1000 ppm (within tannery effluent range), and at flow rates 3 and 8 ml/min: 5 ppm (within drinking water range)

3.5 Filtration test

The concentration of Cr (III) in the filtrates of different samples in different conditions is shown in Fig. 6.

According to Fig. 6, in the case that the concentration of feed solution is 5 ppm (which is more than the maximum concentration of Cr (III) ions in drinking water of different areas in Iran), when the flow rate of the pump is 8 ml/min, only 66% of Cr(III) ions are rejected with sample B-Ca20, but when the flow rate is 3 ml/min, the rejection is increased to 95% which declares the effect of time and indicates that the dominant mechanism is adsorption, because membrane filtration mechanisms are dependant on the size of ions and not on the time. Besides, these samples are in the range of microfiltration membranes (0.1-10 μm pores) and can't reject the Cr (III) ions (0.061 nm) by size.

It can be also seen that in the case that the concentration of feed solution is 1000 ppm, which is more than the concentration of Cr (III) in most of the tannery effluents (Stoller *et al*. 2013, Ranganathan and Kabadgi 2011, El Khalfaouy *et al*. 2017, and Krishanamoorthi 2009), with flow rate of 0.3 ml/min, it can be seen that sample B has rejected 13.9% of Cr (III) ions while sample B-Ca20 successfully removed Cr (III) ions to 99.97%, and decreased the Cr (III) ions concentration from 1000 to 0.2684 ppm. According to the literature (Strathmann 2011, Ranganathan and Kabadgi 2011), microfiltration can't remove dissolved ions such as Cr (III) due to the size limitation, hence the Cr (III) removal here is attributed to the adsorption mechanism.

Calcium alominosilicate phases (including anorthite) (Hoff 2003, Klosek-Wawrzyn *et al*. 2013, Djomgoue and Njopwouo 2013, Garcia Sanchez *et al*. 1999 and Okada *et al*. 2003) and pyroxenes (including wollastonite) tend to adsorb heavy metals in their structures, which is said to be due to the presence of SiO_2 and CaO (Zhao *et al*. 2017). Wollastonite is widely used in removal of heavy metals (Ziegler 2000, Babel and Kurniawan 2003, Bhatnagar and Minocha 2006 and Panday *et al*. 1986).

According to Fig. 6, in sample B-Ca20, as a result of the presence of wollastonite together with increasing the

amount of anorthite, comparing to sample B, the Cr (III) removal is increased from 13.98% to 99.97% (86% increasing). Comparing the approximate amounts of phases (Table 4) it can be said that wollastonite adsorbs much more Cr (III) than anorthite and so is much more effective in Cr (III) removal.

4. Conclusion

• Low cost clay-based adsorptive microfiltration membranes were successfully synthesized.

• Addition of calcium carbonate lead the porosity to increase and despite starch and other organic pore formers, didn't lead to collapse the mechanical strength due to the formation of high duty phases.

• Sample B-Ca20 could successfully remove 99.97% of Cr (III) ions from high polluted water (containing 1000 ppm Cr (III) ions).

• Wollastonite (a pyroxene) and anorthite (an aluminosilicate) play the role of adsorbent and the former seems to be much more effective.

• These adsorptive membranes are suitable alternatives for nanofiltration membranes (which need high pressure pumps), adsorptive nano particles (which need separation after use) and hybrid systems (which are costly) and lead the filtration cost to decrease.

5. Conflicts of interest

Authors have no conflicts of interest to disclose.

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