Ceramic Ultrafiltration and Nanofiltration Membrane for Removal of Black Carbon Ink, Blue Dye Ink, Fe^{3+} and Cu^{2+} Ions from Water

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Abstract

This paper reports on performance of ceramic ultrafiltration and nanofiltration membrane to remove carbon ink particles, blue ink dye, Fe^{3+} and Cu^{2+} ions from water. The ceramic filters have α-Al_2O_3 flat-sheet supporter, with TiO_2 nanoparticles sintered membrane on the surface of supporter. Carbon ink particles, blue ink dye, $FeCl_3$ and $CuSO_4$ water solution were used to test their filtration performance. The results show that the ceramic ultrafilter can 100% decolored the black carbon solution. The nanomembrane can 100% decolored blue ink dye, $FeCl_3$ and $CuSO_4$ solution. Electrical conductivity rate of iron-flocculated dye waste water from a textile company can be reduced by the nanomembrane from 4000 μs/cm to 1000 μs/cm. It assumed that the ultramembrane pore size is about 10 nm, and the nanomembrane pore size might be 1 nm. The performance can fulfill the requirements for removal of heavy metal ions, materials with molecule bigger than 250 Dalton and salts retention from water, air filtration of novel corona virus defending mask and negative pressure patient room.

1. Introduction

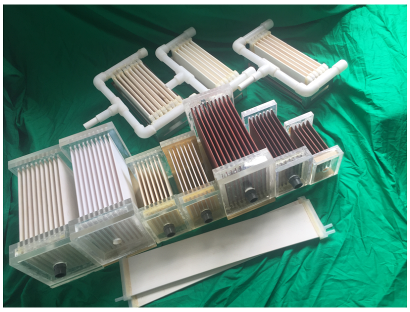
Ceramic filtration membrane is sintered with inorganic material such like α-Al_2O_3, γ-Al_2O_3, ZrO_2, SiO_2, TiO_2, Fe_2O_3, SiC, etc. These materials can resist chemical corrosion, heat, and abrasion in comparation with organic membrane. These make ceramic membrane longer service time, and relative lower total application cost. Ceramic filtration membrane comprises with ceramic supporter, middle layer and top layer. The ceramic supporter is sintered generally with Al_2O_3 particles at over 1400 °C, which have pore size from 3 to 20 micrometer. The middle and top layer can be any above-mentioned materials sintered at lower temperature. The top layer has the finest particles and pores, which is the filtration membrane and determine the filtration pore size.

Ceramic filtration membrane is widely used in materials separation from liquid or air in many industries, especially in food, medicine, chemistry, biology and environment sectors. But the quantity of implementation is still low, because the implementation cost is relatively higher compared with organic membrane. Another issue to prevent ceramic membrane from large scale usage is complexity of fabrication technologies, which is hard to keep the product pore size under control, especially for nanomembrane.

There are numerous researches about ceramic filter synthesis, characterization, and performance testing in lab scale. However, prototype scale testing for industrial usage is not so much. In addition, the heavy metals wastewater treatment using ceramic filtration membrane is rarely reported. This paper shows the result of carbon ink particles, blue ink dye, iron and copper salts removal from water, for investigation of pore sizes and performance of the ceramic membrane before industrial implementation.

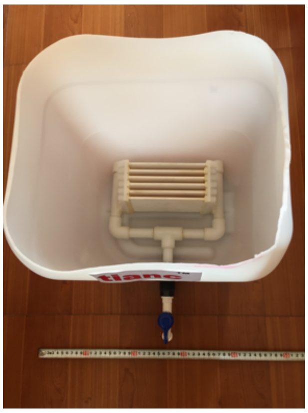
2. Material and methods

Ceramic Ultra and Nano filtration Membrane. The flat-sheet ceramic filtration membrane with registered trade mark "TIANC" was developed and fabricated by Zhejiang Tian Cheng Environmental Co., Ltd in Shaoxing, China. The dimension of a plate of filter is normally 500mmX100mmX6mm. The filtration area is about 0.1 m^2. It can be cut to required size. Water comes from the surface outside into the channels inside to flow out. The picture 1 shows the TIANC ceramic membrane with various surface materials and sizes. These include micro-, ultra- and nanomembrane, with sintered membrane material of TiO_2, ZrO_2, and Fe_2O_3. The Fe_2O_3 membrane was fabricated using green synthesized iron-polyphenols complex nanoparticles technologies that we reported before [1, 2]. It is also the first one which can suit commercial scale usage.



Picture 1. Ceramic filter with various membrane materials including TiO_2, ZrO_2, and Fe_2O_3.

A ceramic membrane module is put at the bottom of a polypropylene container. The liquid is poured into the container, which can penetrate the membrane and supporter of the ceramic filter under gravity. The filtered water comes out from the internal channels to tape head connected with the filter. The picture 2 shows the outlook of the filtration device.



Picture 2. Filtration device with ceramic filter module.

Electrical Conductivity Meter and Reagents. The electrical conductivity meter is DDS-11A type from Leici Shanghai. Black Carbon and blue ink were purchased from a local store, manufactured by Shanghai Hero Group. $FeCl_3$ and $CuSO_4$ in analytical degree were purchased from Marcklin website.

Characterization with Scanning Electron Microscopy (SEM) have been done at the early stage of development of the ceramic membrane. For the reason of cost saving and resolution limitation of SEM, identifiedable material with color were used to investigate the filtration capacities when developing ultra- and nanomembrane. Adsorption effect of ceramic particles has been considered. All filtration results were taken after lasting filtration after one day.

3. Results and Discussion

Ultrafiltration of Carbon Ink Particles. Black carbon ink contains carbon particles with the smallest size of 10 nm [3]. 10-15 mL ink was poured into a container with 25-30 L tap water. It was observed that the black colour water can be totally decoloured. It assumed that the pore sizes of the TiO_2 membrane is about 10 nm, although the ink contains several addictive materials. The flow rate is about 18 L m^{-2} h^{-1} at this situation.

Picture 3. Black carbon ink solution filtration by ceramic membrane.

Nanofiltration of Blue Ink Solution. The blue ink contains acid blue 93 with dye molecular weight of 799.80 Dalton. 10-15ml ink was poured into a container with 25-30 L tap water. The colour of filtered water can also be totally decoloured. It can be assumed that the pore sizes of the Fe_2O_3 membrane is about 1-2 nm without consideration of effects from several addictive materials in ink. The flow rate is about 5 L m^{-2} h^{-1} at this situation.

Picture 4. Blue ink solution filtration by ceramic membrane.

Nanofiltration of Fe^{3+} and Cu^{2+} Ions. Nanofiltration is widely in salts retention, mainly for multivalent ions salt. The mechanism for separation can be explained in terms of charge effects (Donnan theory) and/or size effects (channel theory) [4]. Until now we have not done any test about electron charge, therefore we cannot testify if Donnan theory suits this membrane. Generally speaking, channel theory can be suitable for filtration. $FeCl_3$ and $CuSO_4$ are turned to $FeCl_3•6H_2O$ and $CuSO_4•5H_2O$ in water. Their molecule weights are 270 and 250 Dalton separately. From the picture 5 we can see the filtered water from 0.1 mol/L $FeCl_3$ and $CuSO_4$ solution is very clear. It was 100% decolored. The flow rate is about 2 L m^{-2} h^{-1} at this situation.

Picture 5. $FeCl_3$ solution filtration by ceramic membrane (Left); $CuSO_4$ solution filtration by ceramic membrane (Right).

A test was also done in a textile wastewater treatment. The wastewater has been treated with large amount of iron flocculant. The main issue is to decolour the water to meet the emission requirement to the wastewater treatment facilities in the industrial park. The picture 6 showed that the ceramic membrane can decolour the wastewater well, and can also reduce water electrical conductivity from 4000 μs/cm to 1000 μs/cm. It assumed that the pore size of the membrane is about 1 nm. The flowrate stays at the same speed from the beginning for several day without pause or backwash. In addition, the surface of ceramic nanomembrane can be easily cleaned.

Picture 6. Textile wastewater filtration. Filtered water in beaker, wastewater in glass can (Left photo); Electrical conductivity measurement. From up to down are wastewater, filtered water with ceramic membrane, treated water with reserve osmosis membrane (Middle photo); Membrane surface cleaning (Right photo).

4. Conclusions

The ceramic filtration membrane can remove black carbon ink particles, blue ink molecules (799 Dalton), Fe^{3+} and Cu^{2+} ions from water. That indicated the ultrafiltration membrane have less than 10 nm pore size, the nanofiltration membrane may have 1 nm pore size. The removal of Fe^{3+} and Cu^{2+} ions may be due to the formation of $FeCl_3 \bullet 6H_2O$ and $CuSO_4 \bullet 5H_2O$ in water, which have much bigger sizes than the ions alone. Different salts can verify flow rate of membrane, this may have connection with Donnan and channel theories. Due to small pore size (about 1 nm) the ceramic nanomembrane surface is not contaminated easily and can be cleaned well. It assumed that most particles are bigger than the pores, cannot block the pores easily. This reduces the operation cost of membrane which increased by fouling. Recently novel corona virus (COVID-19) is outbreaking in China, and to the world gradually. The size of virus is about 100 nm [5] . Therefore, the ultra- and nanoceramic filter can be put in breath mask, patient negative pressure room for air filtration, or in water container for drinking water filtration to defend the virus outbreak.

References

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