Quantum Dots Ceramic Nano Membrane for Copper Mining Water Treatment, Turning Na_2SO_4 to NaOH and Pretreatment for Seawater Desalination

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Abstract

This paper reports on performance of ceramic nanofiltration membrane to treat copper mining water, waste salt recycling and purification of seawater. The ceramic filters have α-Al_2O_3 flat-sheet supporter, with sintered TiO_2, Fe_2O_3, or ZrO_2 nanoparticles as membrane on the surface of supporter. The membrane has photoluminescence phenomenon when irradiating with UV lamp. It indicates that they are quantum dots material, whose sizes may be between 2-10nm. The Nanofilter can remove more 90% contaminants from copper mining water. It shows good functional stability in the corrosive mining water. It is also able to turn Na_2SO_4 to NaOH by adding $Ca(OH)_2$. This provides a novel technology to reuse waste salt. The ceramic nanofilter can remove all suspended solid from seawater to ease the subsequent desalination of seawater with reserve osmosis membrane.

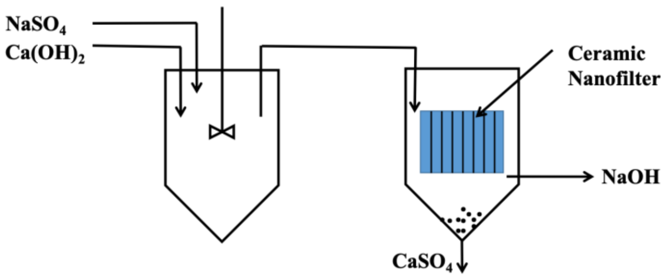
1. Introduction

Heavy metals contaminated water treatment is still a challenging technical issue until today, especially for mining and plating water. The commonly used technologies such as chemical sedimentation cannot reduce the heavy metal ions concentration to emission requirements. Electrodialysis is not suitable for extreme chemical circumstance in mining or plating wastewater. Reverse osmosis membrane cannot undergo heavy metals wastewater continuously because the organic membrane can be reacted or clogged by heavy metal complexes leading to an irreversible membrane damage. 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., which can resist chemical corrosion, heat, and abrasion. If filter has enough filtration precision, it will have potential to remove heavy metals from water.

In addition, million tons of Na_2SO_4 are produced as by-product from many chemical industries each year in China. The traditional waste treatment technologies like landfill and incineration are not suitable for such amount of waste salt. As nanomembrane can withhold divalent ions and let monovalent ions through, the following reaction may happen when adding $Ca(OH)_2$ and energy:

$$\mathbf{Na_2SO_4+Ca(OH)_2 \xrightarrow{\text{Nano Filter}} Na^{+}+(OH)^{-}+CaSO_4\downarrow}$$

Generally speaking, it cannot produce strong alkaline with weak alkaline. With help of nanofilter and additional energy such as gravity, the nanofilter may let Na^+ and OH^- go through, but withhold Ca^{2+} and SO_4^{2-}, which form sediment (see picture 1). Therefore, it is worthful to investigate if the reaction may take place in reverse direction.



Picture 1. Diagram of turning Na_2SO_4 to NaOH using ceramic nanofilter.

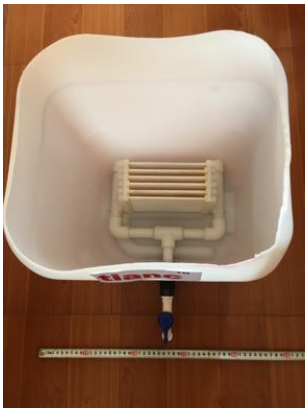
Seawater desalination become a more important way to produce drinking water, especially in dry area like middle east. The main streams technologies are reverse osmosis

(RO) membrane and evaporation. RO is more popular. However, fine suspended matters like cells and metal complexes may clog RO membrane. Using very fine sand filter, active carbon filter or organic nanofilter cannot solve the problem. This reason restricts wide application of seawater desalination worldwide. Now ceramic nanofilter provides a possibility to remove most cells and metal complexes from seawater to reduce clogging for subsequent RO membrane desalination.

2. Material and methods

Ceramic Nano filtration Membrane. The flat-sheet ceramic filtration membrane was fabricated by author based on the principles of green synthesized nanoparticles [1, 2]. 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 flows from the surface through the membrane and supporter into the channels inside and then let out. The membrane material can be TiO_2, ZrO_2, Fe_2O_3 or other ceramic materials.

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 1 shows the outlook of the filtration device.

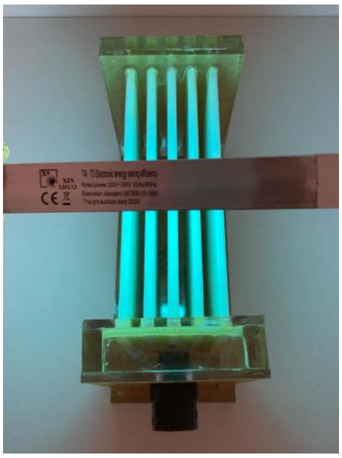


Picture 2. Filtration device with ceramic filter module.

Electrical Conductivity Meter and Materials. The electrical conductivity meter is DDS-11A type from Leici Shanghai. Na_2SO_4 and $Ca(OH)_2$ have been purchased as usual chemical analysis reagents. The UV lamp is PHILIPS 4W UV-C model made in Poland, which have the main emission at 254 nm. Mining water was taken from the copper mining well of Shaoxing Pingtong Group Co., Ltd. Seawater was taken from Daishan island, Zhejiang, China. All filtration results were taken after lasting filtration after one day as adsorption effect of ceramic particles considered.

3. Results and Discussion

Photoluminescence of Nanomembrane. The TiO_2 membrane showed strong cyan-green fluorescence when irradiated with the UV lamp. The cyan-green fluorescence has a wavelength at about 530 nm. This indicated the membrane absorbed UV light energy and emitted green light. This phenomenon is called photoluminescence, which is one character of quantum dots. It assumed that the size of most TiO_2 particles are around 2-10 nm. Therefore, the pore size of the membrane may be under 1 nm, as the pores are channels among sintered particles. At the same time, the TiO_2 quantum dots may work as photocatalyst with UV light to degrade some organic matters in water or air.



Picture 3. The TiO_2 membrane showed strong cyan-green fluorescence when irradiated with the UV lamp. This is photoluminescence phenomenon.

Treatment of Mining Water with Nanomembrane. These heavy metals wastewater from mining or plating cannot be treated by reverse osmosis membrane directly after sand or active carbon filtration. The reason is heavy metals can damage the RO organic membrane. It assumed that the heavy metals react with organic membrane, or metal complex clogs membrane.

The mining water taken from mining site had red brown color and pH=2.4. The contaminants and their concentrations in the water are shown in the table 1. The water has been adjusted pH to 6 using $Ca(OH)_2$ firstly, then went through the ceramic filter. The analysis results (table 2) showed that the nanofilter had reduced sulfide from 8990 to < 0.005 mg/L (more than 99% reduction), fluoride from 24.2 to 0.90 mg/L (96% reduction), copper from 215.0 to 13.5 mg/L (94% reduction), zinc from 717.0 to 68 mg/L (91% reduction). The treated water is colorless with reduced CODcr to 28. The water can be reused as mineral separation water. Otherwise it can be treated further with reverse osmosis or electrodialysis membrane to meet the emission requirements. As the mining water is corrosive and turbid, the ceramic nanofilter should be the best option for its treatment, which also make further treatment using reverse osmosis or electrodialysis membrane possible. The flow rate of the nanofilter by gravity is about 0.2L/h*M^2.

Copper Mining Water	
pH	2.4
Electrical Conductivity (μS/cm)	7300
Suspended Substance (mg/L)	5
Total dissolved solid (mg/L)	13900
Sulfate (mg/L)	8990
Fluorides (mg/L)	24.2
Ca (mg/L)	403
Na (mg/L)	66.6
Mg (mg/L)	473
Al (mg/L)	435
Fe (mg/L)	932
Mn (mg/L)	22.4
Cu (mg/L)	215
Ba (mg/L)	0.06
B (mg/L)	0.002
Zn (mg/L)	717
As (mg/L)	0.035
Sr (mg/L)	4.57
Hg (mg/L)	<0.001
Pb (mg/L)	0.0036
Active Silicon (mg/L)	57.8

Table1: Mining water quality from mining well.

Water after Nano Filtration (mg/L)	
CODcr	28
TN	5.48
TP	0.02
NH3-N	1.86
Fluorides	0.90
Zn	68.0

Sulfate	<0.005
Cu	13.6

Table2: Water quality after filtration by ceramic nanofilter.

Emission Standard	
pH	6-9
Suspended Substance (mg/L)	80
CODcr	60
Fluorides (mg/L)	5
TN	15
TP	1.0
NH3-N	8
Zn	1.5
Total petroleum hydrocarbon	3.0
Cu	0.5
Sulfate	1.0
Pb	0.5
Cd	0.1
Ni	0.5
As	0.5
Hg	0.05
Co	1.0

Table 3: Water discharge requirements.

Turn Na_2SO_4 to NaOH using Nanomembrane. Na_2SO_4 solution has been made to have concentration of 0.5 mol/L in the container. Then the same mol $Ca(OH)_2$ was put in the Na_2SO_4 solution. The water after filtration was clear and no $CaCO_3$ membrane on the water surface formed. This means the ceramic nanofilter removed significant amounts of Ca^{2+} ions. The water before and after filtration had the same pH of 12, but the electrical conductivity decreased. It assumed that the OH^- remained at the same concentration, but electrical charges were reduced. It indicated the Na_2SO_4 can been turned to NaOH through the ceramic nanofilter with addition of $Ca(OH)_2$.

The pH and electrical conductivity are influenced by filter pore sizes, concentration of Na_2SO_4 and $Ca(OH)_2$. It was also observed that pH value increased along with time passing by. This also means that more NaOH produced after filtration.

Feasibility of Pretreatment of Seawater Desalination Using Ceramic Nanofilter. The muddy seawater became very clear and bright after filtration by the ceramic nanofilter. There was no tyndall effect observed by irradiating the filtered water with laser pen. In addition, the nanofilter has been approved by our last report that it can remove 780

Daltons acid blue dye [3]. It assumed that the water quality may suit the requirement of RO membrane for further treatment. The electrical conductivity of seawater had no obvious change after treatment. It assumed that seawater should add some flocculant to make Ca^{2+} and Mg^{2+} suspended solid particles or complexes before nanofiltration.

4. Conclusions

The TiO_2 membrane of the ceramic nanofilter showed strong cyan-green fluorescence when irradiated by UV lamp. The photoluminescence phenomenon indicates the membrane are composed of quantum dots, which particle sizes are between 2–10 nm. The quantum dot materials make the filter pore sizes to 1 nm of diameter or smaller possible. This membrane fabrication method also provided a new approach to produce quantum dot materials. The nanofilter can remove more 90% contaminants from mining water. It resists to the corrosive heavy metals contaminated wastewater and show excellent stabile filtration capability. It also provided a novel technology to turn waste salt Na_2SO_4 to NaOH by adding $Ca(OH)_2$. The ceramic nanofilter may achieve a high purification capability for pretreatment of seawater desalination, which make the feedwater more clean and ease the subsequent RO system operation.

References

1. Wang, Z., *Iron Complex Nanoparticles Synthesized by Eucalyptus Leaves*. ACS Sustainable Chemistry & Engineering, 2013. **1**(12): p. 1551-1554.
2. Wang, Z., C. Fang, and M. Megharaj, *Characterization of iron–polyphenol nanoparticles synthesized by three plant extracts and their fenton oxidation of azo dye.* ACS Sustainable Chemistry & Engineering, 2014. **2**(4): p. 1022-1025.
3. Wang, Z. and T.C. Wang, *Ceramic Ultrafiltration and Nanofiltration Membrane for Removal of Black Carbon Ink, Blue Dye Ink, Fe3+ and Cu2+ Ions from Water.* 2020.