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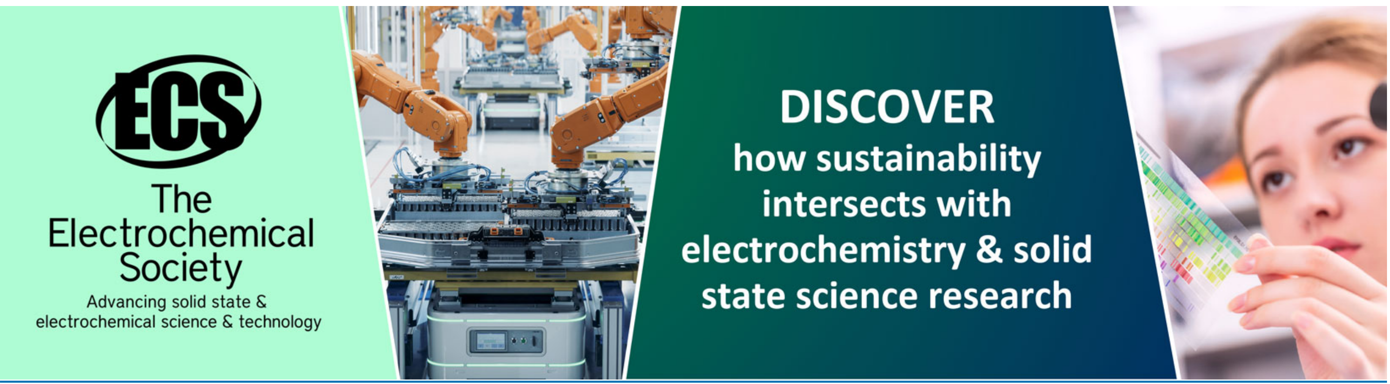

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Recovery of chromium using membrane containing charged material

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Abstract: Chromium (Cr) is one of the important materials of metal family with large applications in formation of ferrous alloys viz., steel. Due to its excellent chemical, mechanical and thermal properties it is largely used in mineral, leather tanning, dye, steel, and other alloy industries. Effluents of these industries containing traces of Cr are polluting water bodies and soil in surrounding. It would result in entering in food chain, where it has highly adverse effect on humans, animals, and environment. Hence its recovery from effluent and other streams is highly essential before disposal and exposure to surrounding. The polysulfone (PSF) based membranes were optimized using polyethylene glycol (PEG) as porogen, while ZnO as an additive either treated with or without acid for removal of Cr from water. A reduction in molecular weight of PEG resulted in decrease in water flux indicates reduction in pore size. Further incorporation of ZnO increases the Cr removal. The Cr removal increases further with incorporation of acid treated ZnO. Additionally, HCl treated ZnO showed higher rejection properties, while the effect is not that prominent in HNO_3 treated ZnO. This shows the importance of optimization of membrane surface charge for heavy metal removal.

Keywords: Polysulfone, polyethylene glycol, zinc oxide nanoparticle, chromium ion, rejection, permeation

1. Introduction:

Chromium (Cr) is one of the important metals due to its excellent chemical, mechanical and thermal properties. It is one of the most widely distributed metal ions in the earth's crust [Sivakumar S. et al 2005]. This wide availability and excellent properties lead to large applications of Cr in chemical and other industries for the formation of reactors and other systems. Though the stability and other properties are attractive, it poses some limitations on processibility and shaping. It can be used as an important component of alloys like stainless steel [Ray S. et. al. 2009]. Moreover, it is also used in plating on metal/ plastic materials, decorative or protective automotive, equipment coating, and in nuclear and high-temperature research [Bazrafshan E. et al. 2015, Fu F. et al. 2011, Shanker A. K. et al. 2005]. Hence the large quantity of Cr is extracted from minerals or recycled for the formation of these materials. During these extractions, recovery and recycle treatments, a large amount of Cr found its way to effluent and waste disposal. According to Ray et. al. (2009), 4500 kg/day of chromium was released in the environment due to different processes in the U.S.A.

Cr is present in nature in chromite ($FeOCr_2O_3$) form. It has three oxidative states Cr (II), Cr (III), and Cr (VI). Cr (III) is comparatively less harmful, approximately 500 times less than Cr (VI) as it has low water solubility [Alam N.E. et al. 2020, Ray S. et al. 2009]. The effects of industrialization and subsequent human activities like metal processing, electroplating, leather tanning, chemical production, paint, pigment, dye industries are releasing large quantities of Cr through effluent [Bazrafshan E. et al. 2015, Fu

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F. et al. 2011]. This is resulting in large scale Cr contamination in environment-water and, soil. This contamination is adding to natural activities like weathered rocks, volcanic exhalations, biogeochemical processes, which is making the situation worse. These metal ions have tendency of accumulation and cause plant/ soil poisoning and disorder in liver, lung, kidney, brain, central nervous system functioning. Further, human exposure to Cr activates teratogenic processes, causes cancer, disturbs DNA synthesis, mutagens changes- malignant tumors, kidney, liver, gastric damage, nasal irritation/ ulcer, and fluctuates urinary level. It changes soil microbial populations and metabolism, affects the photosynthesis process, alters the germination process, affects the growth of roots, stems, and leaves [Ray S. et al. 2009, Bazrafshan E. et al. 2015, Singh H.P. et al. 2013]. Hence various limitations are defined by WHO for its permissible limit in the disposal stream. Cr maximum contaminated level (MCL) by USEPA is 0.05 mg/L [Gunatilake S. K. 2015].

Metal ions *viz.* arsenic, chromium, copper, iron, nickel, sodium, zinc, etc. are important at low concentration for normal growth/ functioning of human, animal, plant, and soil biota. Its consumption in higher quantities can cause serious health issues by interfering with normal body functioning. Hence it highly essential to control heavy metal pollution by human activity. Hence recovery or removal of Cr from the various process and effluent disposal streams is highly essential.

Various conventional methods are available for the separation of heavy metals such as chemical-precipitation, ion-exchange, adsorption, coagulation, flocculation, flotation, electrochemical, and advanced-membrane separation methods [Fu F. et al. 2011]. Conventional methods have good separation efficiency but have the issues of generation of a secondary pollutant, recovery issues restrict their applicability. Hence, there is a need for a reliable techno-economical, environment-friendly, sustainable separation, and recovery method. Membrane-based methods *viz.* reverse-osmosis (RO), nanofiltration (NF), electrodialysis (ED), ultrafiltration (UF) has ability to treat heavy metal containing water for component recovery without chemical contamination [Mahajan-Tatpate P. et al. 2021]. They have benefits of physical recovery of a component without addition of chemicals. Hence the recovered components can be recycled back/utilized in further processes. But RO, NF membrane operating pressure is high, and it can remove essential components such as monovalent Na^{+}, and divalent Ca^{+2} which are essential for the normal growth of human beings. Whereas ED process needs clean feed and regular cleaning and monitoring. UF membrane operates comparatively at low pressure and considering secondary treatment process involved in conventional process, it is cost comparable. Hence UF membranes are utilized for heavy metal separation. But there is a need for optimizing the membrane properties for the desired separation with a high transport rate to make the process techno-economically beneficial along with ecological benefits. For this purpose, the present study focuses on optimizing the membrane transport and Cr rejection properties with the use of PEG as pore forming agent and ZnO as rejection improving additive. The effect of dope solution composition on transport rate and Cr rejection is investigated.

2. Materials and Methods:

2.1. Materials:

Reagents used in the present study are all synthesis-grade chemicals. Polysulfone (PSF) was procured from Otto Chemie Pvt. Ltd., N, N'-Dimethyl acetamide (DMAc), and Polyethylene glycol (PEG) with molecular weight 1500 (PEG-1500) was purchased from Loba Chemie Pvt. Ltd. India. PEG with molecular weight 400 (PEG-400), 600 (PEG-600) were procured from High Purity Lab. Pvt. Ltd. India, and 6000 (PEG-6000) was procured from Sisco Research Lab Pvt. Ltd. Zinc oxide (ZnO) nano powder of size 80-100 nm was procured from Nanoshel LLC. Hydrochloric acid (HCl) and Nitric acid (HNO_3) were procured from Merck Ltd. India. Non-woven polyester backing 3324 was procured from Ahlstrom Hollytex. Potassium dichromate was procured from Sisco Research Laboratory.

2.2. Method of Membrane Preparation:

PSF based porous membranes were prepared by the phase inversion method. The casting solution was prepared by dissolving 29 % PSF (w/v) and 8% PEG (w/w of PSF) in DMAc as discussed earlier [Dhume S. et al. 2020]. It is followed by dispersing 0.8% ZnO nano powder optionally treated with acid (HCl or HNO_3) in the formed solution. The formed solution is degassed to remove dissolved air and used for casting on non-woven polyester backing 3324. Water is used as a non-solvent, at ambient temperature. An automatic membrane casting machine (Shivom membrane casting system) was used to prepare membrane. The formed membrane samples were stored and maintained at 4°C before use in flux, and rejection property analysis.

3. Characterization:

3.1. Water Flux Analysis:

The water flux of the prepared membrane was measured at 2 bar pressure using a dead-end cell, at room temperature. The water transport rate/ flux was measured using Eq. 1.

$$J = \frac{V}{A \times \Delta t} \tag{1}$$

Where, V is a volume (Liter) of water transported across the membrane in time (Δt, hour) through the membrane of cross-sectional area (A).

3.2. Chromium ion Rejection Analysis:

For chromium ion rejection analysis, a 1000 ppm solution of potassium dichromate was prepared. This solution was passed through the membrane and permeate was collected. Chromium ion retained on the membrane was determined by collecting permeate and its analysis was done by double beam UV visible spectrophotometer (UV 3000^+ from Lab India) by measuring absorbance at 313 nm. Percent rejection (% R) was calculated by

$$\%R = \left[1 - \frac{C_p}{C_f}\right] \times 100 \tag{2}$$

Where C_p and C_f is the concentration of permeate and feed respectively.

4. Result and Discussions

4.1. Effect of molecular weight of PEG on Pure Water Flux:

PSF based membranes prepared using the phase inversion method showed a large effect of dope solution concentration on transport properties. An increase in dope solution concentration leads to a reduction in pore size [Phale J. S. et al. 2015]. It resulted in increased polyethylene glycol (MW 6000 Da) (PEG 6000) rejection, desired property for heavy metal (Cr) removal. It also leads to a reduction in water flux which would affect the separation economy.

Further use of PEG is reported as pore forming agent for PSF based membranes, which affects the hydrophilicity and transport properties of formed membranes [Dhume S. et al. 2020]. It is highly soluble in water, which can be leached by water used as a gelation agent during membrane formation. Such leaching would result in the formation of pores at the place of PEG in membranes. This increases the porosity of the membrane by maintaining pore size, which results in increase of pure water flux while maintaining selectivity or rejection properties for PEG 6000 [Dhume S. et al. 2020]. The increase in transport rate and maintaining rejection properties are attributed to the formation of the pore by removal of PEG [Chakrabarty B. et al. 2008]. It is reported that with decrease in molecular weight of PEG, water flux decreases, which attributes to a decrease in pore size of the membrane, which is desired property for current work to improve rejection of metal ion. Hence, it was thought that a reduction in PEG molecular weight would help to improve the transport rate while improving the rejection properties.

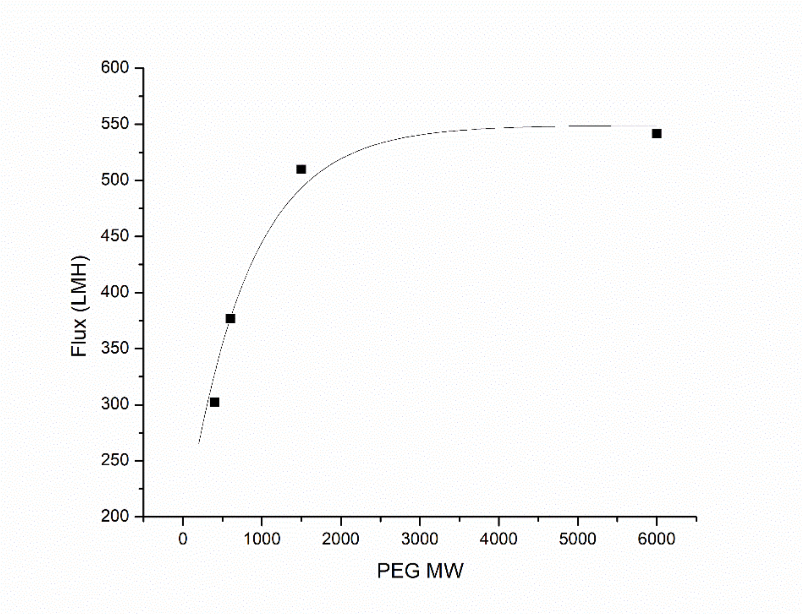

Figure 1. Effect of PEG molecular weight on Pure Water flux

PEG with different molecular weights ranging from 400 to 6000 was used to prepare the membrane. Formed membranes were analyzed for water flux to determine the effect of PEG molecular weight on transport properties of porous membranes [Fig.1]. The membrane flux (302 to 541 LMH) increases logarithmically with an increase in PEG molecular weight. This could be attributed to a reduction in pore size which increases resistance for transport of water across the membranes. It was observed that with a decrease in molecular weight of PEG, pure water flux has decreased. It attributes to a decrease in pore size with a decrease in molecular weight. [Kim J.H. et al. 1998, Chakrabarty B. et al. 2008].

4.2. Effect of acid treated ZnO nanoparticle on chromium ion rejection:

It was well reported by Chung Y.T. et al. 2015 that nano sized ZnO is effectively used to remove heavy metals from water. ZnO nanoparticles improve water flux, which means it forms a more porous structure of the membrane and it also helps to improve rejection. The equal distribution of these metal nanoparticles in dope solution improves PSF membrane hydrophilicity and decreases its fouling [Chung Y. T. et al. 2015]. Polysulfone membrane performance has improved by the addition of ZnO nanoparticle even for CO_2, CH_4 separation [Moradihamedani P. et al. 2013]. Leo C.P. 2012 stated that the hydrophobic nature of PSF membrane has changed to hydrophilic by addition of ZnO nanoparticles which results in reduction in the fouling of membrane. Also, it increases the thermal stability of the membrane. [Leo C.P. et al. 2012].

Membrane prepared with PEG-400 has the minimum water flux as compared with high molecular weight PEG. The rejection properties for chromium ions were studied on a membrane prepared with PSF/PEG 400/ZnO. The addition of ZnO has shown improved membrane properties. Here in this study, ZnO was modified with acid treatment.

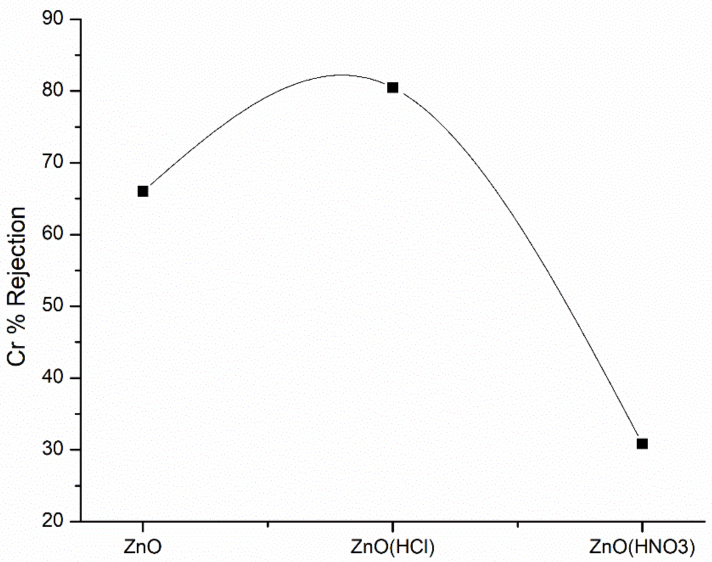

Figure 2. Effect of Modified/ unmodified ZnO incorporated membrane on % Rejection

ZnO nanoparticle reacts with HCl and produces $ZnCl_2$. This $ZnCl_2$ reacts with polysulfone, this interaction gives surface charge to the membrane [Mukherjee R. et al. 2015]. The addition of $ZnCl_2$ in dope solution decreases membrane roughness and membrane become smoother, results in a decrease in pore size of membrane [Mondal M. et al. 2015, Panda S.R. 2014]. Here the $ZnCl_2$ binds with the PSF by weak interaction between strong chloride ions and PSF molecules. Thus, it will provide a charge to membranes. The potassium dichromate solution has a negatively charged dichromate anion. According to the Donnan exclusion principle, there is repulsion between similar charge ions. So, there is repulsion between membrane surface and chromium ions. The presence of Zn would provide the repulsive interactions with metal ions enhancing the rejection properties. Thus, the rejection property of membrane cast with ZnO modified with HCl increases from 66 to 80%. This can be attributed to increase in Zn ionization in chloride format which would improve the Donnan rejection properties for Cr.

A curious case was observed when the ZnO was modified with HNO_3, the rejection of Cr was reduced from 66 to 38 % for the membrane containing virgin ZnO and ZnO modified with HNO_3, respectively. This can be attributed to formation of zinc nitrate during the interaction between ZnO and HNO_3. Here the negative charge of N and membrane is masked by the presence of O_3. It would reduce the interactions and repulsion of similarly charge Cr and in turn the rejection properties.

5. Process Implementation and Economy:

Chromium is one of the major pollutants in various industries including cement where it is found in different oxidation states like 3, 4.6, 5, 6, etc. [Sinyoung S. et al. 2011, Estokova A. 2018]. The leachate material is one of the major sources of heavy metal pollution in cement industry. Further, a tannery industry releases a large amount of chromium in the effluent stream used for leather tanning [Alam N. E. et al. 2018, Alam N. E. et al. 2020]. It is also a part of effluent generated from steel/metal plating, automobile, battery manufacturing, refinery, pharmaceutical, as observed from the industrial zones of Balanagar, Hyderabad. Here sediments from conventional effluent treatment units contain chromium up to 96.2 to 439.6 mg/kg [Machender G. et al. 2014].
For these effluent treatment conventional effluent treatment methods *viz.* chemical precipitation, ion-exchange, adsorption, coagulation, electrocoagulation, flocculation, flotation, electrochemical, etc. used, require chemical addition for heavy metal separation. During process it can generate toxic intermediate compound. This hazardous sludge if not treated further, can cause secondary pollution, and has disposable issues. Formed complexes or separated phase needs further treatment for regeneration and recovery of metal ions. This generated secondary sludge, which affects the economy and real-life applicability of those processes.
Further, some of the advanced technologies like membrane-based methods *viz*. RO, NF, ED, UF is available to treat the wastewater from those industries [Alam N. E. et al. 2020]. Some of these methods show good separation efficiency based upon physical separation and recovery methods without any addition of chemicals. They have limitations towards design of membranes and energy intensive processing due to high pressure applications (RO, NF), electricity driven processes (ED), etc.
Ultrafiltration based membrane separation possesses benefits of higher transport rates and low energy requirements. They can be used at moderate process conditions and combined with conventional process streams for continuous separation of metal ions, its recovery and recycling of other desired streams. They need the membranes to be designed carefully for obtaining desired selectivity properties while maintaining transport rate. This would provide techno-economic benefits along with continuous recovery and recycle of heavy metals. This would enhance the benefits further. Considering all limitations of conventional separation methods and RO. NF, ED membrane-based methods, use of surface-modified UF membranes provide multiple benefits about its commercial implementation and process enhancement for recovery of metal ions in pure form.

6. Conclusion:

Chromium is an important material in different industrial application along with part of various processes in the form of chemical compositions. During these processes and material formation large amount of Cr is released to environment through effluent and waste streams. This along with the natural activities enhances its concentration in water and soil biota. Where it can prove to be detrimental to human, animal, soil, and environment if its concentration is above standard permissible limit. It possesses the properties of bioaccumulation which makes it more dangerous upon entry into food chain. Hence it is highly important to control its release to environment through human activity. Though various processes have been reported for its treatment conventional separation processes have limitations of addition of chemicals and generation of intermediate compound which needs disposal or secondary treatment. Membrane based processes physically separate metal ions in nascent form without any change in chemical property. RO and NF have high operational cost and removes the desired components from water. UF membrane is techno-economical and sustainable considering all aspects, but it requires careful membrane optimization for desired transport and selectivity properties. Current work shows PSF based membranes modified with PEG as porogenic agent and ZnO (alternatively treated with acid) shows excellent (80 %) recovery of Cr ions, with excellent transport properties at low operational pressure (2 bar). This makes the membranes techno-economically feasible and environmentally attractive choice for treatment of process streams for Cr removal before their release or disposal to the atmosphere.

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