REJECTION MECHANISM FOR ARSENATE, CHROMATE AND PHOSPHATE IONS VIA POLYACRYLONITRILE ULTRAFILTRATION MEMBRANE

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by

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Certificate

This is to certify that the thesis entitled "**Rejection Mechanism for Arsenate, Chromate and Phosphate Ions via Polyacrylonitrile Ultrafiltration Membrane**" being submitted by Muthumareeswaran M.R. is worthy of consideration for the award of the degree of Doctor of Philosophy. The thesis has been prepared under my supervision and guidance in conformity with the rules and regulations of Indian Institute of Technology Delhi and is a record of the original bonafide research work. The results presented in this thesis have not been submitted in part or full to any other universities or institutes for the award of any other degree or diploma.

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Abstract

ABSTRACT

Development of effective and economical techniques for removal of heavy metals and inorganic pollutants from drinking water and wastewater has always been a great concern for environmental as well as process engineers. The presence of heavy metals like arsenic, chromium and large amount of phosphate in aquatic source, and eventually in potable water, is a serious health issue. Membrane separation technology is a viable and highly innovative process engineering operation which can be applied for heavy metals and inorganic pollutant removals from aquatic stream. The main advantages of membrane techniques are low energy consumption, no chemical reaction and separation in the continuous mode. Conventional membrane technologies like Reverse Osmosis and Nanofiltration require high operating pressure for water treatment as compared to Ultrafiltration membrane.

Chromium and arsenic are the sixth and twentieth most abundant element respectively in earth's crust. Generally, the heavy metals contamination in water occurs due to natural phenomena such as the presence of minerals, volcanic emissions; human activities like wood preservatives, fertilizers, industrial processes and waste treatment. On the other hand, the existence of large amount of phosphate in domestic and industrial wastewater causes the eutrophication which is a serious environmental issue in water sources. Thus, removal of arsenic, chromium and phosphate from water streams is very important from both environmental and economic points of view.

The present study is to investigate the polyacrylonitrile based UF membrane for effective and selective removal of arsenic, chromium and phosphate from water. Applicability of polyacrylonitrile (PAN) based ultrafiltration (UF) membrane for effective arsenic, chromium and phosphate removal was established, to our knowledge, for the first time. PAN based UF membrane surface was hydrolyzed by 1 N NaOH and it led to the formation of carboxylate (COO^-) groups

which reduced the pore size to improve divalent anionic rejection capability. The pore size reduction was assessed by lowering in water flux and increase in PEG and proteins rejection. The membrane structural parameters such as mean pore radius, porosity, pore size distribution and roughness were determined by atomic force microscope (AFM), whereas iso-electric point and charge density of membrane surface were measured by tangential streaming potential (TSP) measurements. Solution pH was directly correlated with the membrane structural properties like porosity, pore size distribution and these parameters were directly proportional to the volumetric flux whereas the membrane roughness was inversely proportion to the flux.

The removal of anions (arsenate, chromate and phosphate) from potable water using surface modified polyacrylonitrile ultrafiltration membranes was carried out with plate and frame module in cross-flow mode. Ultrafiltration membranes and their different coupons were subjected to anionic concentrations in the feed ranging from 250 ppb to 1000 ppm to test its efficacy. The effects of physical and engineering parameters (pressure, temperature and cross flow velocity) as well as chemical parameter (ions concentration and pH) on the rejections of anions were studied as a function of time. Variation of feed pH played a vital role on ions transport through the membrane. More than 95% rejection of arsenate, chromate and phosphate ions were achieved separately for each anions at pH ≥ 7. The electro neutrality condition was also confirmed by counter-ion (sodium ion) rejection which was also more than 90% at pH ≥ 7. The concentration polarization was negligible at low feed concentration (≤ 150 ppm). But concentration polarization effect was found at higher concentration of each divalent anions (≥ 200 ppm) and the rejection of arsenic, chromium, phosphate ions were found to be in the range of 45 % to 72% at high cross-flow velocity and low transmembrane pressure.

The rejection mechanism of anions was strongly dependent on Donnan exclusion principle. Generally, higher rejection % of arsenate, chromate and phosphate ions (≥ 92%) were obtained with high Donnan potential value (~ 20 mV). Moreover, Donnan potential was vital at feed concentrations (1 ppm to 150 ppm) and it was negligible at very low feed concentration (<<1000 ppb) and again it became weaker at very high concentration (≥ 500 ppm).

In multicomponent system, the mixture of arsenate, chromate and phosphate ions showed more than 92% for feed concentration of 50 ppm each. However, the arsenate rejection decreased to 55–60% for 5 ppm arsenate and 50 ppm each of chromate, phosphate mixture in the feed, while chromate and phosphate rejections remained ≥90%. The change in proportion of feed concentration in multicomponent system like 50 ppm of arsenate along with 5 ppm of chromate and 5 ppm of phosphate ions resulted more than 90 % of As (V) but Cr (VI) and PO_4^{2-} rejection coefficients were reduced to 70% and 74% respectively. Moreover, the retention of anions through modified PAN UF membrane, was also dependent on hydrated radii of the solute and the rejection of anions followed the order Cr (VI) <As (V) < PO_4^{2-}. In addition, heavy metals (arsenate, chromate) and phosphate removal using polyacrylonitrile ultrafiltration, were effective (≥ 97%) at low pressure operation compared to nanofiltration (NF) membranes.

The surface modified membrane were also subjected to high operating transmembrane pressure for the effective removal of arsenic, chromium and phosphate ions from potable water. The membrane showed more than 94% rejection efficiency of divalent anions at the transmembrane pressure of 10 bar. The surface modified polyacrylonitrile membrane was not showing any fouling and would work for a long time; gave almost 100% rejections for ppb level concentration of arsenate and ppm level of chromate, phosphate ions in the feed. However, due to concentration polarization effect on the membrane surfaces, the rejection % of arsenate, chromate and phosphate ions were reduced to 87 %, 85% and 89% respectively at 12 bar of transmembrane pressure.

The removal of arsenate, chromate and phosphate ions through modified PAN UF membrane were also subjected to other ions (such as nitrate, sulphate, carbonate, calcium and sodium chloride) which are normally available in ground water. The rejection % of arsenate, chromate and phosphate ions were reduced to 70 % to 78% in the presence of other ions in the feed.

The Donnan steric-partitioning pore model incorporated with dielectric exclusion (DSPM-DE) model was applied to evaluate the ions transport through the membrane as a function of flux by using optimized model parameters like feed concentration, the membrane active layer thickness, the effective volumetric charge density and membrane permeability. The modified DSPM DE model was applied for theoretical calculation of flux and rejection of arsenate ions in the case of PAN membrane. The model also applied for chromate and phosphate ions rejection through the membrane. The comparison of simulated and experimental rejection data showed that DSPM-DE model fully predicted the tendencies and pattern of ionic rejection as a function of flux.

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