Fabrication of fly ash based ceramic membrane for tomato juice clarification and water treatment

Thesis submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

By

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Introduction

Coal fly ash from the combustion of raw coal in thermal power-plants is a source of dust which adversely affects our environment. Presence of toxic constituents in fly ash such as hazardous metals, polycyclic aromatic hydrocarbons and silica can have adverse effects on human health. Hence, it is of utmost necessity to decrease environmental pollution caused by fly ash and at the same time produce a high added-value product from it. Presently, it is of great interest to prepare membranes from low cost abundant raw materials available worldwide. Porous ceramic membranes have excellent thermal, chemical, and mechanical resistances and hence they have been widely employed in many industrial separation applications. Being rich in Al_2O_3 and SiO_2, fly ash can thus be used as a precursor for the fabrication of dense mullite - based ceramics.

Ceramic membranes can be utilized for numerous applications. Two such applications include juice clarification and water treatment. Microfiltration (MF) requires lower energy, capital costs and is a non-thermal separation methods which causes no phase change and minimal loss of proteins, vitamins, sugars and salts and ultra-filtration during the clarification of various juices. Hence, the properties of the juice remain intact unlike treatments using enzymes and fining agents. Microfiltration using ceramic membrane is also used for the treatment of contaminated drinking water and industrial effluents. This process in combination with other techniques can be an effective method for increased efficiency. The main advantages in juice clarification is the non-requirement of any supplementary chemicals addition. To enhance the process of microfiltration, agglomeration of toxic pollutants from aqueous solutions can be carried out using electrocoagulation process. Electrocoagulated byproducts can then be filtered through a ceramic membrane to obtain contaminant free and non-turbid water.

Objectives of work

This thesis is focused on microfiltration membrane preparation using fly ash as the major precursor and its use in vegetable juice clarification and water treatment. The main objectives are

- To prepare and characterize fly ash based ceramic membranes for tomato juice clarification in batch mode.
- To fabricate a thermo-responsive polymer coated ceramic membrane.
- To prepare and characterize a novel adsorbent from tomato waste for the treatment of Co (II) contaminated water.
- To use the prepared microfiltration membrane for the treatment of fluoride contaminated drinking water using electrocoagulation followed by microfiltration.
- Treatment of drilling effluents using electrocoagulation followed by microfiltration using ceramic membranes prepared from fly ash.
- Treatment of NF reject water from steel plant using electrocoagulation followed by microfiltration.

Organization of the thesis

In order to fulfil the above objectives the thesis is organized in eight chapters. The content of each chapter is given below.

Chapter 1 addresses the state of the art, research motivation of present work, possible scope of research, objectives and organization of the thesis. **Chapter 2** discusses the application of fly ash based low cost membranes for the clarification of tomato juice in batch mode operation. Various resistances existing during the microfiltration process were studied along with an analysis on the quality of the treated juice. The prepared fly ash based membrane was modified by a polymer layer coating and discussed in **Chapter 3**. A composite ceramic membrane was prepared and a thermo-responsive polymer Poly (2-ethyl-2-oxazoline) was dip coated. The fabricated composite membranes were characterized and applied in the filtration of BSA protein. **Chapter 4** describes the utilization of waste generated after tomato juice clarification (Chapter 2) to prepare an adsorbent for the removal of Co (II) contaminated water. **Chapter 5** describes the application of selected fabricated membrane in **Chapter 1** for the microfiltration of electrocoagulated by-product obtained during treatment of Fluoride contaminated drinking water using electrocoagulation. **Chapter 6** presents the application of the fabricated ceramic membrane for the microfiltration of electro coagulated drilling fluids for the removal of oil, grease and other heavy metals. In addition to a detailed characterization, studies were also done on the corrosion and operating costs of the electrocoagulation process. **Chapter 7** presents the application of the prepared membrane in the microfiltration of electrocoagulated Nanofiltration reject water from the steel industry**.** Finally, **Chapter 8** contains the inferences drawn from various chapters presented in this thesis and some suggestions towards scope for future work.

Abstract

The present work discusses a simple and easy method for the preparation of ceramic membrane suitable mainly for microfiltration applications. The prepared ceramic membrane was modified using a temperature responsive polymer to prepare a specially surface modified ceramic membrane. Various applications carried out in the present work include microfiltration of tomato juice, treatment of fluoride water, treatment of steel industry wastewater, treatment of drilling wastewater, utilization of carrot water from microfiltration process into a novel adsorbent for the treatment of Co (II) contaminated water.

Fly ash based ceramic membranes having a varying pore size were prepared using the paste casting method. Three different membranes MB1, MB2 and MB3 were prepared with pore sizes 20-21µm, 1-2.29 µm and 227-450 nm, respectively. The membrane thus prepared were used in the clarification of tomato juice to eliminate pectin like compounds responsible for deteriorating its quality with time. The resistance-in-series model was used to evaluate the decline in flux of tomato juice during microfiltration. The contribution of fouling resistance was in between 98% and 96%, adsorption resistance 0.09% to 0.33%, pore plugging resistance from 0.33% to 0.91% and membrane resistance from 0.6% to 2% of overall total resistance. The fouling resistance was thus found to be the main resistance involved in the flux decline of all the three membranes.

The prepared ceramic membranes were then surface modified using a special temperature responsive polymer poly (2-ethyl-2-oxazoline). Different parameters such as polymer concentration (5 - 20 wt. %) and dip coating time (20-60 s) were considered while preparing the membrane. Temperature responsiveness was utilized for studying the variation in water flux and BSA rejection. For temperatures above LCST (lower critical solution temperature)

the flux achieved was highest at about 5.58 × 103 L/h.m^2 than at temperatures below LCST. A very good rejection of 68% was observed for membrane M-15 (coated with 15 wt. % polymer). Hydraulic permeability of the membrane M-15 decreased with an increase in dip coating time and increased with an increase in operating temperature.

The waste from the clarification of tomato juice in the previous work was utilized in the preparation of a novel adsorbent for the treatment of Co (II) contaminated water. Adsorbents from organic wastes such as tomato and carrot were prepared by chemical activation method. To increase their adsorption capacity the prepared adsorbents were combined with PET bottle leftovers to create a new composite adsorbent. An optimum adsorbent dosage of 1.2, 0.6 and 0.8 g/L for ACW, ATW and APTC respectively was found to give the maximum amount of adsorption. The effect of all the three adsorbents on the physicochemical properties of Co (II) adsorption was studied by varying different parameters such as contact time, adsorbent dose and pH. Kinetic behavior of the three adsorbents for the uptake of Co (II) were studied. Freundlich model was best suited for the composite adsorbent with an adsorption capacity 312.50 mg/g.

The prepared ceramic membranes were also utilized in the field of treatment of fluoride contaminated drinking water in combination with the electrocoagulation process. Three samples of drinking water with fluoride concentration of 7.89, 4.79 and 1.78 mg/L were collected from the hand tube well located in Karbi Anglong, Assam. The contaminated water was first pretreated using the electrocoagulation technique. Effect of current density in the range of 15, 10 and 5 A/m^2 and an inter-electrode distance of 0.005 m was considered. A decrease in concentration to 0.0097, 0.335 and 0.656 mg/L for initial fluoride concentration of 1.78, 4.79 and 7.89 mg/L respectively were observed. The pretreated water was then transferred to a microfiltration setup consisting of the previously prepared ceramic membrane. Filtration studies suggested an increase in flux from 287.28 to 690.84 $L/m^{2}\cdot h$ when the pressure increased from 196 to 509 kPa. Produced flocks were characterized to confirm the presence of fluoride. The proposed hybrid technique was able to reduce the fluoride concentration of contaminated drinking water to below permissible limit of 1.5 mg/L (WHO).

The prepared ceramic membrane were also utilized in the treatment of oil water effluents collected from a drilling site in Barekuri, Assam. Effluent water from the drilling site having oil and grease along with metals like Na, Cr, Cu, Pb and Ni were treated using the electrocoagulation technique by varying the current density (20-80 A/m^2), electrode distance (0.005-0.2 m) and initial pH (3.6-8.7). The concentration of oil and grease was reduced from 35 mg/L to 10.2 mg/L in just 25 min. TDS values decreased from 3230 to 2780 mg/L. Conductivity of the feed increased from 2.65 to 6.19 which was due to the addition of NaCl, salinity remained more or less the same. Trans-membrane pressures were maintained at three different pressures of 98,196 and 194 kPa. At a pressure of 98 kPa the permeate flux increased from 264 to 423 $L/h.m^2$ when sintering temperatures increased from 700 to 1000^oC. It was also observed that 75-85 % of the initial flux was lost during the microfiltration of the electrocoagulated samples. The electrode cost and energy cost increased with increasing current density. The total cost as a result increased from 0.0502 to 0.253 US$/m^3 when current density increased from 20 to 80 A/m^2. Flocks produced during the EC process were characterized using FESEM, EDX, XRD and FTIR.

Reject water from steel industry had chloride, sodium, potassium, manganese, magnesium, pH, TDS, sulphate, calcium and iron. This reject water was treated by a lab scale batch process of electrocoagulation followed by microfiltration of the electro-coagulated sample. The microfiltration process utilized a membrane prepared from fly ash. Removal studies were performed considering the operating parameters current density, run time and electrode distance. At a current density of 50 A/m^2, inter-electrode distance of 0.005 m and run time of 20 min the concentrations of Na, Mg, K and Ca were reduced to 449, 54, 35 and 18 ppm respectively, whereas Mn and Fe were found to be completely removed. The TDS concentrations were lowered to 2100, 2092 and 2070 ppm from an initial concentration of 2530 ppm at current densities of 20, 30 and 50 A/m^2. A detailed study was also done on the corrosion of the electrodes and the operating cost of the electrocoagulation process. Microfiltration studies were carried out at pressures of 103, 117 and 196 kPa. Membrane resistance contributed to about 71.8 % of the total offered resistance. Produced flocks were analyzed using EDX to confirm the removal of the metals by the electrocoagulation process.

List of Publication

Published:

1. V.L. Dhadge, C.R. Medhi, M. Changmai, M.K. Purkait, "House hold unit for the treatment of fluoride, iron, arsenic and microorganism contaminated drinking water" **Chemosphere** 199 (2018) 728-736.

2. M. Changmai, P. Banerjee, K. Nahar, M.K. Purkait, "A novel adsorbent from carrot, tomato and polyethylene terephthalate waste as a potential adsorbent for Co (II) from aqueous solution: Kinetic and equilibrium studies" **Journal of Environmental Chemical Engineering** 6 (2018) 246-257.

3. M. Changmai, M.K. Purkait, "Detailed study of temperature-responsive composite membranes prepared by dip coating poly (2-ethyl-2-oxazoline) onto a ceramic membrane" **Ceramics International** 44 (2018) 959-968.

4. M. Changmai, J.P. Priyesh, M.K. Purkait, "Al2O3 nanoparticles synthesized using various oxidising agents: Defluoridation performance" Journal of Science: Advanced Materials and Devices 2 (2017) 483-492.

5. M. Changmai, M.K. Purkait, "Interaction of fatty acid chain length with NiFe2O4 nanoparticles" Surfaces and Interfaces 8 (2017) 45–53

6. M. Changmai, M.K. Purkait, "Kinetics, equilibrium and thermodynamic study of phenol adsorption using NiFe2O4 nanoparticles aggregated on PAC" Journal of Water Process Engineering 16 (2017) 90–97.

Under review:

1. M. Changmai, M. Pasawan, M.K. Purkait, " A hybrid method for the removal of fluoride from drinking water: Parametric study and Cost estimation" **Journal of Environmental Management** (Under review)

2. M. Changmai, M. Pasawan, M.K. Purkait, "Treatment of drilling effluent using electrocoagulation followed by microfiltration" **Journal of Hazardous materials** (Under review)

3. M. Changmai, M.K. Purkait, "Fly ash based membrane fabricated from mechanically varied precursor powder for the clarification of tomato juice: Resistance-in-series model" **Journal of Food Science and Technology** (Under review)
4. M. Changmai, M. Pasawan, M.K. Purkait, "Treatment of steel industry effluent using a hybrid technique". (Ready for submission)

Conferences/ Seminars or workshops

1. M. Changmai, P. Banerjee, K. Nahar, M.K. Purkait, "A novel adsorbent from carrot, tomato and polyethylene terephthalate waste as a potential adsorbent for Co (II) from aqueous solution: Kinetic and equilibrium studies" Indo- Japan bilateral symposium (IJBS) on Future Perspective of Bio resources "in North-East India", 1-4 February 2018, Indian Institute of Technology Guwahati.

2. M. Changmai, M. Pasawan and M.K. Purkait, "A hybrid method for the removal of fluoride from water" 7th International conference on Chemical, Agriculture, Environment and Natural Sciences (CAENS-2017), 20-21 November 2017, Kuala Lumpur, Malaysia.

3. M. Changmai and M.K. Purkait, Fly ash based membrane for the clarification of tomato juice: Resistance-in-series model, REFLUX 2017, 24-26 March, 2017, Indian Institute of Technology Guwahati.

4. M. Changmai and M.K. Purkait, "Defluoridation performance of Al2O3 nanoparticles synthesized using various oxidising agents" International Conference on Nano for Energy and Water (NEW) Indo French Workshop on Water Networking 2017), 22-24 February, University of Petroleum and Energy Studies Dehradun.

5. M. Changmai and M.K. Purkait, "Effect of fatty acid chain length on the structural properties of the coated NiFe2O4 nanoparticles" International Conference on Nano for Energy and Water (NEW) Indo French Workshop on Water Networking 2017), 22-24 February, University of Petroleum and Energy Studies Dehradun.

6. M. Changmai and M.K. Purkait, "Detailed study on the variation of particle size of precursor powder with pore size distribution of ceramic membranes" Emerging trends in separation science and technology-SESTEC 2016, 17-20 May, 2016, Indian Institute of Technology Guwahati.

7. Course by Indian Institute of Technology Bombay on "Technical Communication for Scientists and Engineers", 11 January - 02 May 2016.

8. M. Changmai and M.K. Purkait, "Microfiltration of tomato juice: Resistance in series model" 3rd Indo-German Workshop on "Advances in materials, reaction and separation processes" 23-26 February, 2016, Indian Institute of Technology Guwahati.

9. M. Changmai and M.K. Purkait, “Investigation on the variation of particle size of precursor powder with pore size distribution of membrane” CHEMCON-2015, 27-30 December, 2015, Indian Institute of Technology Guwahati.