Influence of Unsteady State Dynamics on the Rejection of Cadmium (II) by Ultrafiltration

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ABSTRACT

The unsteady-state permeate flux response to a step change in the transmembrane pressure in a stirred ultrafiltration cell was studied. The changes in the gel-layer concentration and gel-layer growth, with the change in the transmembrane pressure were studied. Metal solutions were prepared in a polymeric solvent, and the dynamics of the operating parameters on this process were studied. The process, a hybrid process called Polymer Enhanced Ultrafiltration, (PEUF) was modeled mathematically and validated using experimentation for the change in the transmembrane pressure and concentration of the polymeric solvent added. The permeate flux was modeled using gel-polarization model and first principles model which was solved using MATLAB’s PDE and ODE solver subroutines.

Keywords: Ultrafiltration, PEUF, fouling, gel-polarization, unsteady-state, mathematical model

1.0 INTRODUCTION

The term “ultrafiltration” (UF) was coined to discriminate this process from separation by filtration, where much larger particles are separated (> 1 μm). The ultrafiltration membrane process, which was initially developed for the treatment of wastewaters and sewage, is now widely used in various applications in industries such as automobile (electrocoat paint), food and dairy (sugar refining, vegetable oils, corn, fruit juices, wine and beer, fluid milk, cheese and whey) and biotechnology (enzyme recovery, membrane bioreactors) industries. A detailed review of such applications has been done by Cheryan et al. (1998) [1]. Many polymers have been used for ultrafiltration (UF) membrane material such as cellulose acetate (CA), polyacrylonitrile (PAN), polyethersulfone (PES), polysulfone (PS) and polyamide. In case of UF membranes, the polymer material should exhibit excellent biocompatibility and comparable low cost. Moreover, they should also possess good film forming ability and an appropriate morphology. Amongst these polymeric materials, cellulose acetate has always been used as the basic material for UF membranes with their maximum uniformity, permeability, selectivity and optimum physical properties such as strength and flexibility.

In spite of wide applications in the aforementioned fields, radical application has been limited due to the phenomenon of concentration polarization and membrane fouling. Even though the process holds promise of separation efficiencies above 95%, the industry still faces challenges due to this phenomenon. The phenomenon
of membrane fouling causes the pores to clog with retentate particles and cause a decline in the permeate flux. For this reason alone there has been tremendous research to control the fouling occurring in such pressure driven filtration units. Generally, the treatment of fouled membrane units is based on the type of fouling occurring. Reversible fouling can be taken care of by physical methods (periodic back washing, forward washing, flow pulsations and promotion of turbulence by gas permeation) or chemical methods like (chemical cleaning, feed treatment). Feed pretreatment has gained considerable focus in the recent years due to the sheer simplicity of its application. Addition of a chemical to the feed (before it is sent into the unit as the feed) and treating it is the main idea behind this method. Precoagulation (coagulant), in-line coagulation systems (in-line dosing of coagulants), Flocculation systems (floculant), Complexation-Ultrafiltration (complexing agent), Micellar Enhanced Ultrafiltration (surfactant), Polymer Enhanced Ultrafiltration (Polymeric Ligand) are some of the exemplary methods that employ this method of fouling control [2]. After the addition of the said agents, the feed is then appropriately treated and sent in as a feed to the UF unit. Many industries including chemical, electronic, metal plating and refining industries face severe problems in the disposal of their waste streams when highly toxic or valuable constituents such as metal ions are present [3]. From these waste streams heavy metals such as Cd (II), Cr (VI), Cr (III), Cu (II), Zn (II), etc., could be separated and concentrated through the binding of the target metal ions to water-soluble polyelectrolyte and subsequent ultrafiltration of the bound metals from the unbound components [4]. Water-soluble polymers are commercially available as ligand to bind with metal ions. Among the most important technological requirements are the follows: those polymers are the high solubility in water, chemical stability, high affinity for one or more metal ions, and selectivity for the metal ion of interest [5]. Mimoune et al. [Mimoune] studied the separation of metal ions using PVA as a polymeric ligand. The use of other polyelectrolytes like pDADMAC (poly-DAllyl DiMethyl ammonium Chloride) [6] for Copper, chitosan [7] and PEI (Poly Ethylene Imine) [8] have also been well documented.

The advantages of PEUF include high removal efficiency, high binding selectivity and highly concentrated metal concentrates for reuse, etc. The basic idea here is to understand the dynamics of the process of Polymer Enhanced Ultrafiltration (PEUF) on the basis of an unsteady state model [9]. We give a step change in the TMP and check the variation in the permeate flux and metal ions concentration in the permeate with respect to time. A resistances-in-series-model was proposed to simulate this process and to predict the flux and permeate concentration variations with changes in the TMP.

1.1 Unsteady State Flux Modeling

Oers et al. reported experimental stirred cell UF data for Dextran and Silica using totally retentive membranes [10]. They measured the permeate flux as a function of time for sudden variation in the TMP. However their measurements were based on long times, so there were unaccounted changes in the variations of the bulk properties of the sample feed, which masked the unsteady state flux properties. From the time scale of this work, it was inferred that the gel layer formation takes a lot longer than the
formation of the polarization layer. The concentration polarization layer takes a matter of seconds to few minutes to form; the gel layer takes near about more than an hour to form. The mathematical model that they had designed was mainly focusing on the change in the permeate flux and solute concentration at the membrane wall due to the change in the bulk properties, i.e. bulk concentration, and bulk volume.

Karode had worked on the same lines as van Oers, validating his model for a shorter time scale and undertaking a parametric study of the process [11]. That work consisted mainly of flux prediction based on the first principles model. In this work the system was run for a cycle of pressure changes. The feed system taken was a gel-forming species and a non-gel forming species. As soon as the steady state flux was attained, a step change (plus or minus) in the TMP was given to the system. The resulting flux decline was monitored. The mathematical model prepared from the first principles model was solved for simulating the flux decline for the experimental conditions. The primary difference between the model prepared by van Oers et al. [10], and Karode were that Karode’s model [11] simplified the solution by implementing dimensionless parameters instead of the actual parameters, thus making the limits of the operating parameters vary from 0 to 1, hence simplifying the way the initial and boundary conditions were applied to the system. This work focuses on modeling the phenomenon of PEUF based on unsteady state flux model proposed by Karode and checking the performance of the membranes based on flux and rejection of the solute. The TMP, ΔP is changed as soon as a steady state of flux is reached, the permeate sample is taken for analysis at the beginning of a pressure run and another sample at the end of such a pressure run. This helps us in finding out the effect of increasing/decreasing ΔP during each pressure run. It was also theorised that the concentration of the permeate would vary based on the previous pressure cycles in the ultrafiltration cell.

The suitable membrane materials were selected on its separating property, for good performance in the separation/retaining of metallic solutions in the ultrafiltration process. The unsteady state flux decline for an unsteady state ultrafiltration process for separation through CA, modified CA and modified PAN membranes was performed. The performance of the selected membranes for the separation of metal ions solution of Cadmium Sulphate Octahydrate (3CdSO₄.8H₂O), by the process of PEUF by using pDADMAC (poly-DiAllyl DiMethyl Ammonium Chloride) polymeric ligand was performed. effects of transmembrane pressure cycles and the ligand concentration in the metal ions present in the system also studied.

2.0 MATERIALS AND METHODS

2.1 Choice of the Membranes

The membranes used for this process were selected on the basis of their resistive capability. A hydrophilic membrane is capable of giving more pure water flux than a hydrophobic membrane based on the solution-surface interaction as defined earlier. The membranes selected for the separation here are CA, modified-CA and modified-PAN. The modification in the membranes is done by the addition of Kaolinite, mineral clay, to the membrane solution before casting.
it. Kaolinite has a low shrink-swell capacity and a low cation exchange capacity (1-15 meq/100 g), thus decreasing the surface activity of the membrane surface. Due to this reason alone, it enhances the hydrophillicity of the membranes and causes to increase the pure water flux of the membranes. CA membrane is modified by the addition of egg-shell membrane powder to membrane solution, to increase the hydrophillicity of the CA membrane.

2.2 Choice of the Solution System

In order to validate the modeling done, experimental analysis is inevitable. The separation of metal ions from aqueous solutions was taken up to study the modeling done for the flux analysis. A solution of 1000 ppm (1 g/L) Cadmium Sulphate Octahydrate (3CdSO₄·8H₂O) was made in 3 concentrations of pDADMAC solvent, 0.2%, 1% and 3%. The pH of the solution was maintained around 4.6.

The feed solution is undergone filtration in Cellulose Acetate (CA), modified CA and modified Polyacrylonitrile membranes (PAN) membranes. All the experiments were done at constant stirring speed, as the higher rotation speeds causes the formation of vortex and the mixing is non-uniform. The newly prepared membrane is compacted with pure water for 1 hour, measuring the pure water flux. Then the feed solution is charged, and while the filtration process is going on, permeate samples are collected at the starting of each pressure run and steady state flux value, in order to analyze the rejection of metal-chelates, using an Atomic Absorption Spectrophotometer. After the run, pure water flux is measured again, which will give us the idea about the extent of fouling happened during the filtration process.

A single run for an experiment commences with the applied pressure at a constant value, where a sample of the permeate is taken for analysis. After the steady state flux (constant value of flux) is achieved, we take another permeate sample and give a step change in the pressure is given so as to keep the system in a state of unrest, i.e. unsteady state. Permeate samples are collected at the commencement and steady state value of each pressure step, thus giving us the amount of rejection at the beginning and the end of each pressure step. The flux value is monitored continuously during the course of the experiment for changes with respect to step changes in the TMP.

2.3 Experimental Setup

The setup consists of a dead-end ultrafiltration cell, Solvent-Resistant™ stirred cell from Millipore Inc., USA Model XFUF 076 (76 mm diameter), equipped with a pressure pump, Millipore High Output™ pump, (max pressure 80 psi), from Millipore Inc., USA. The cell is designed to withstand upto 90 psi pressure. With a membrane diameter of 76 mm and a maximum holdup volume of 300 ml, the setup is capable of providing effective surface areas of ~40 cm². This cell is placed on a magnetic stirrer and the stirring speed is placed between the optimum values of 200 r.p.m.-300 r.p.m. so that no vortices can form. The permeate is collected in a separate beaker after the commencement of the experiment. Flux is calculated with the help of graduated cylinders constantly. The quality of the permeate is analyzed using Atomic Absorption Spectrophotometer (AAS) (Thermo Scientific™ ice 3000). The amount of solute rejection is calculated from the concentrations of the feed and the permeate. Bulk viscosity of the
permeate and retentate are checked using viscometer to check for any changes in the viscosity of the feed solution through the course of the experiment and are found to be ~1.34.

2.4 Experimental Procedure

A concentration of 1000 ppm. of aqueous metallic solution was prepared in the polymer solvent (of concentrations 0.2 wt. %, 1 wt. %, 3 wt. %). The variation of metal ion concentration, polymer solvent concentration, pressure cycles and membrane material for unsteady state dynamics is shown in Table 1. This solution was made to stand over for sometime (~30 minutes) for the metal ions to bind with the polymeric ligand and form metal chelates. The batch of the resulting solution is taken and fed to the UF cell for the separation process. The flux is continuously monitored till steady state value is achieved and at that point a step change is given in the ΔP, changing the flux values and the metal ion rejection values in the permeate. The step size is 20 psi.

A single batch of feed is run for a cycle of pressure changes, i.e. if we start a certain run at 20 psi pressure, the pressure is changed to 40 psi and 60 psi after the steady state values for flux are reached. The permeate samples are collected for the analysis at the beginning of the run and the steady-state flux value. This is to compare the metal ion separation achieved for the ultrafiltration run done in the UF cell.

Table 1 Variation of parameters for the conducting the experiments

| Sl. No. | Expt. no. | Metal ion concentration (ppm) | Polymer solvent concentration (wt. %) | Pressure Cycles (psi) | Membrane material |
|---------|-----------|-------------------------------|-------------------------------------|----------------------|-------------------|
| 1       | 1         | 1000                          | 0.2                                 | 20                   | PAN-K             |
| 2       | 2         | 1000                          | 0.2                                 | 20-40                | PAN-K             |
| 3       | 3         | 1000                          | 0.2                                 | 40-60                | PAN-K             |
| 4       | 4         | 1000                          | 1                                   | 20-40                | CA                |
| 5       | 5         | 1000                          | 1                                   | 20-60                | CA                |
| 6       | 6         | 1000                          | 3                                   | 20-40                | mod-CA            |
| 7       | 7         | 1000                          | 3                                   | 20-40-60             | mod-CA            |
| 8       | 8         | 1000                          | 3                                   | 20-40-60-20          | mod-CA            |

The details of the runs are given as follows. The separation of 1000ppm CdSO₄ solution in 0.2 wt. % of pDADMAC solution run at 20 psi is shown in Table 2. The run number corresponds to the choice of the solvent concentration and metal ion concentration, selected for feeding into the ultrafiltration cell as a batch for a certain separation.

Table 2 Rejection results for Experiment 1: Separation of 1000 ppm CdSO₄ solution in 0.2 wt. % of pDADMAC solution run for 20 psi

| Sl. No. | Sample ID | Time (mins.) | Pressure (psi) | pH  | Conc. (mg/l) | %SR |
|---------|-----------|--------------|----------------|-----|--------------|-----|
| 1       | 1         | 0-10         | 20             | 4.65| 555          | 44.5|
| 2       | 2         | 70-80        | 20             | 4.65| 437.9        | 56.21|
3.0 RESULTS AND DISCUSSION

The transient flux shows a decline with respect to time when subjected to a constant transmembrane pressure across the membrane surface. This coincides with the theory regarding the initial flux decline after the commencement of the experiment, and it shows that the initial flux decline is because of the formation of a polarization-layer and the attaining of steady state flux is an indication of formation and consolidation of gel-layer. The changes in the initial and final rejection values are calculated accordingly and given as follows. The samples are taken at the commencement of the experiment and at the time when steady state flux is attained.

3.1 Separation of 1000 ppm CdSO4 Solution in 0.2 wt. % of pDADMAC Solution

The concentration polarization layer formed in this experiment is the main cause of decrease in the solvent rejection by the membrane, though the drop in the rejection is not very much. In the Table 3, the separation of 1000 ppm CdSO4 solution in 0.2 wt. % of pDADMAC solution at 20 and psi cycle is presented.

Table 3 Rejection results for Experiment 2: Separation of 1000 ppm CdSO4 solution in 0.2 wt. % of pDADMAC solution run for 20/40 psi pressure cycle

| Sl. No. | Sample ID | Time (mins.) | Pressure (psi) | pH | Conc. (mg/l) | %SR |
|--------|-----------|--------------|----------------|----|--------------|-----|
| 1      | 1         | 0            | 20             | 4.6| 470          | 53  |
| 2      | 2         | 45           | 20             | 4.6| 450          | 55  |
| 3      | 3         | 55           | 40             | 4.6| 420          | 58  |
| 4      | 4         | 145          | 40             | 4.6| 28.7         | 71.3|

The system reaches the critical flux value easily for a feed solution with higher concentration of polymer in the feed. In the sample ID 3 and 4 showed the change in concentration, % SR of PAN-K and CA membranes at 40 psi.

For lengthier pressure cycles, i.e., 20-40-60 psi and 20-40-60-20 psi, the flux values are supposed to revert back to the previous conditions with pressure. The reason for this not happening is clearly attributed to consolidation of the gel-layer formed on the membrane surface. Similarly for a bigger step in the ΔP value (from 20 psi to 60 psi) also fails to present much change on the permeate flux value. Rejection values for the 20-40 pressure cycles. There is no significant changes of rejections at 40 and 60 psi (Table 4). This may be due to change in concentration of CdSO4 solution with 0.2 wt. % of pDADMAC.

Table 4 Rejection results for Experiment 3: Separation of 1000 ppm CdSO4 solution in 0.2 wt. % of pDADMAC solution run for 40/60 psi pressure cycle

| Sl. No. | Sample ID | Time (mins.) | Pressure (psi) | pH | Conc. (mg/l) | %SR |
|--------|-----------|--------------|----------------|----|--------------|-----|
| 1      | 1         | 0            | 40             | 4.65| 526.8        | 47.32|
| 2      | 2         | 55           | 40             | 4.65| 537.86       | 46.214|
| 3      | 3         | 65           | 60             | 4.65| 552.03       | 44.797|
| 4      | 4         | 155          | 60             | 4.65| 559.7        | 44.03|
3.2 Separation of 1000 ppm CdSO₄ Solution in 1 wt. % of pDADMAC Solution

As a significance, pDADMAC are essential to coordinate I ion mol of cadmium. The unsteady state dynamics that influence weight of polymer-metal complex (pDADMAC- Cd) formation, pH and metal rejection. The separation of 1000 ppm CdSO₄ solution in 1 wt. % of pDADMAC solution for 20 and 40 psi pressure cycle is shown in Table 5.

Table 5 Rejection results for Experiment 4: Separation of 1000 ppm CdSO₄ solution in 1 wt. % of pDADMAC solution run for 20/40 psi pressure cycle

| Sl. No. | Sample ID | Time (mins.) | Pressure (psi) | pH | Conc. (mg/l) | %SR |
|---------|-----------|--------------|----------------|----|--------------|-----|
| 1       | 1         | 0            | 20             | 4.8| 149.54       | 85.046 |
| 2       | 2         | 35           | 20             | 4.8| 232.95       | 76.705 |
| 3       | 3         | 45           | 40             | 4.8| 236.05       | 76.395 |
| 4       | 4         | 95           | 40             | 4.8| 420.83       | 57.917 |

The removal efficiency is affected with the bound of Cd metal ions by extent of coagulation of the Cd by pDADMAC. The pDADMAC is a water-soluble polymer widely used as a flocculant in waste water treatment. In this study, pDADMAC is used as binder in Polymer Enhanced Ultrafiltration, (PEUF). The separation of 1000 ppm CdSO₄ solution in 1 wt. % of pDADMAC solution run for 20 and 60 psi pressure cycle (Table 6). PEUF is effective that can separate low-concentration metal ions from aqueous solution.

Table 6 Rejection results for Experiment 5: Separation of 1000 ppm CdSO₄ solution in 1 wt. % of pDADMAC solution run for 20/60 psi pressure cycle

| Sl. no. | Sample ID | Time (mins.) | Pressure (psi) | pH | Conc. (mg/l) | %SR |
|---------|-----------|--------------|----------------|----|--------------|-----|
| 1       | 1         | 15           | 20             | 4.8| 159.39       | 84.061 |
| 2       | 2         | 35           | 20             | 4.8| 228.52       | 77.148 |
| 3       | 3         | 40           | 60             | 4.8| 255.04       | 74.496 |
| 4       | 4         | 50           | 60             | 4.8| 348.8        | 65.12  |

The %SR of 1000 ppm CdSO₄ solution in 3 wt. % of pDADMAC solution run for 20 and 40 psi pressure cycle is presented in Table 7. The pDADMAC is a polyelectrolyte of opposite charge to the target ions, causing the cadmium ions to bind to pDADMAC due to electrostatic attraction to form macromolecular complexes. These pDADMAC- Cd complexes are retained on the membrane as rejection, though the uncomplexed ions transport through the membrane in the permeate.
Table 7 Rejection results for Experiment 6: Separation of 1000 ppm CdSO$_4$ solution in 3 wt. % of pDADMAC solution run for 20/40 psi pressure cycle

| Sl. No. | Sample ID | Time of sampling (mins.) | Pressure | pH | Conc. (mg/l) | %SR |
|---------|-----------|--------------------------|----------|----|--------------|-----|
| 1       | 1         | 5                        | 20       | 4.8| 587.67       | 41.233 |
| 2       | 2         | 60                       | 20       | 4.8| 610.84       | 38.916 |
| 3       | 3         | 75                       | 40       | 4.8| 601.75       | 39.825 |
| 4       | 4         | 150                      | 40       | 4.8| 672.79       | 32.721 |

The relatively high wt% pDADMAC required to substantially increased rejection, allow the use of PEUF with higher rejections. An advantage of removal of cadmium using PEUF, compared to some other pollutants, is that feed concentrations of the cadmium are often quite low. The results presented in Table 8 is to the removal of cadmium ion. UF experiments with 1000 ppm of Cd at pH = 4.8 were performed with 3 wt. % of pDADMAC as the target metal ion. The results are listed in Table 8. In contrast with the 3 wt. % of pDADMAC + Cd systems, the behaviour observed in the UF experiments with significant rejection for the conditions employed in this study.

Table 8 Rejection results for Experiment 7: Separation of 1000 ppm CdSO$_4$ solution in 3 wt. % of pDADMAC solution run for 20/40/60 psi pressure cycle

| Sl. No. | Sample ID | Time (mins.) | Pressure | pH | Conc. (mg/l) | %SR |
|---------|-----------|--------------|----------|----|--------------|-----|
| 1       | 1         | 5            | 20       | 4.8| 587.67       | 41.233 |
| 2       | 2         | 65           | 20       | 4.8| 610.84       | 38.916 |
| 3       | 3         | 80           | 40       | 4.8| 601.75       | 39.825 |
| 4       | 4         | 145          | 40       | 4.8| 672.79       | 32.721 |
| 5       | 5         | 160          | 60       | 4.8| 651.05       | 34.895 |
| 6       | 6         | 200          | 60       | 4.8| 655.22       | 34.478 |

In this work, we could conceptually investigate cadmium rejection at different time and pressures with 3 wt% (Table 9) of ligand (pDADMAC), which specifically complexes the cadmium -containing compound and binds to the pDADMAC. This process is called ligand-modified polyelectrolyte-enhanced ultrafiltration (LM-PEUF) and has been shown to effectively remove cationic heavy metals with high selectivity [11, 12]. The gel layer formed by this concentration polarization which can either increase or decrease solute rejection (SR). The final experiment shows that the flux values are definitively decreased due to the fouling occurring before the final pressure step value.

The final 20 psi cycle flux is lesser than the first 20 psi cycle. This indicates that the membrane has fouled to a noticeably significant state, where
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it alters the steady state flux value as well. The gel-layer has consolidated to a state where reversal of the pressure cycle has no effect on its permeability; hence complete reversibility hasn’t been achieved. The rejection values drop throughout the course of the experiment indicative of the same fact that the fouling is occurring due to both the gel-polarization layer.

Table 9  Rejection results for Experiment 8: Separation of 1000 ppm CdSO₄ solution in 3 wt. % of pDADMAC solution run for 20/40/60/20 psi pressure cycle

| Sl. No. | Sample ID | Time (mins) | Pressure (psi) | pH | Conc. (mg/l) | % SR |
|---------|-----------|-------------|----------------|----|--------------|------|
| 1       | 1         | 10          | 20             | 4.8| 598.78       | 40.122 |
| 2       | 2         | 70          | 20             | 4.8| 604.4        | 39.56 |
| 3       | 3         | 80          | 40             | 4.8| 604.05       | 39.595 |
| 4       | 4         | 120         | 40             | 4.8| 627.54       | 37.246 |
| 5       | 5         | 130         | 60             | 4.8| 661.27       | 33.873 |
| 6       | 6         | 180         | 60             | 4.8| 671.94       | 32.806 |
| 7       | 7         | 200         | 20             | 4.8| 681.36       | 31.864 |
| 8       | 8         | 270         | 20             | 4.8| 684.22       | 31.578 |

4.0 CONCLUSION

Suitable membrane materials were selected, based on their separating property, good performance in the separation/retention of metallic solutions in the ultrafiltration process was achieved. The performance of the membranes was validated for the separation of metal ions solution of Cadmium Sulphate Octahydrate (3CdSO₄·8H₂O), by the process of PEUF (Polyelectrolyte Enhanced Ultrafiltration). The membranes (CA, modified-CA and modified-PAN) gave acceptable performance for the separation of Cd (II) ions by the process of PEUF. The TMP and concentration of polymeric solution in the feed were varied to check the performance of the membranes and effectiveness of the process. The effect of pressure cycles and polymer concentration on the PEUF system were successfully studied by the application of gel-polarization model. Rejection studies and unsteady state flux behaviour for the process and effectiveness were analysed accordingly.

The applicability and validity of gel-polarization model was studied. Hence it was elucidated from the work that the separation of Cd (II) by PEUF using pDADMAC followed the pore fouling mechanism by the gel-polarization model for concentration polarization and membrane fouling. The unsteady state flux studies were matching with the literature reported [11].

The observations can be summarised as follows:

- The system follows concentration polarization layer based performance rather than actual fouling as previously anticipated. The rejection of the solute instead of increasing decreases. This is a clear indicator of the formation of a concentration polarization layer.
- The polarization layer formed is reversible as the performance of
the membrane (flux wise and rejection wise) is retained after reducing the pressure value, which is a sure sign of the formation of the polarization layer and not the fouling layer.

- The rejections are high for low concentration polymer solutions and lower for high concentration polymer solutions. This indicates an inverse relation between the polymer solvent concentration and the rejection value in PEUF for an unsteady state flux study. This observation can further help in modifying presently available gel-polarization models in literature.

Thus the observations made from the above experiments have helped in understanding the dynamics of the unsteady state flux studies of PEUF and give better insight into the functional dependency of not only the operating, membrane and feed parameters but also various other phenomenological parameters which may be helpful in developing a better gel-polarization layer mathematical model to describe the concentration polarization phenomenon in Ultrafiltration process.

REFERENCES

[1] Cheryan, M. 1998. *Ultrafiltration and Microfiltration Handbook*. Technomic Publishing Company, Inc.

[2] Verma, Satya Pal, and Biswajit Sarkar. 2018. Simultaneous Removal of Cd (II) and p-cresol from Wastewater by Micellar-enhanced Ultrafiltration using Rhamnolipid: Flux Decline, Adsorption Kinetics and Isotherm Studies. *Journal of Environmental Management*. 213 (2018): 217-235.

[3] Nakhjiri, Ali Taghvaie, Hamidreza Sanaeepour, Abtin Ebadi Amooghin, and Mohammad Mahdi A. Shirazi. 2022. Recovery Of Precious Metals from Industrial Wastewater Towards Resource Recovery and Environmental Sustainability: A Critical Review. *Desalination*. 527 (2022): 115510.

[4] Muller, J., Ding, X., Geneste, A., Zajac, J., Prelot, B. and Monge, S. 2021. Complexation Properties of Water-soluble Poly (vinyl alcohol)(PVA)-based Acidic Chelating Polymers. *Separation and Purification Technology*. 255:117747.

[5] Bediako, John Kwame, Jong-Won Choi, Myung-Hee Song, Che-Ryong Lim, and Yeoung-Sang Yun. 2021. Self-coagulating Polyelectrolyte Complexes for Target-tunable adsorption and Separation of Metal Ions. *Journal of Hazardous Materials*. 401(2021): 123352.

[6] Mimoune, Scheherazade, Rafik Eddine Belazzougui, and Farouk Amrani. 2007. Purification of Aqueous Solutions of Metal Ions by Ultrafiltration. *Desalination*. 217(1-3): 251-259.

[7] Crini, Gregorio, Nadia Morin-Crini, Nicolas Fatin-Rouge, Sebastien Deon, and Patrick Fievet. 2017. Metal Removal from Aqueous Media by Polymer-assisted Ultrafiltration with Chitosan. *Arabian Journal of Chemistry*. 10(2017): S3826-S3839.

[8] Metecan, Ayşe, Aydin Cihanoğlu, and Sacide Alsoy Altinkaya. 2021. A Positively Charged Loose Nanofiltration Membrane Fabricated through Complexing of Alginate and
Polyethylenimine with Metal Ions on the Polyamideimide Support for Dye Desalination. *Chemical Engineering Journal.* 416(2021): 128946.

[9] Huang, Yifeng, Jennifer Du, Yufeng Zhang, Darren Lawless, and Xianshe Feng. 2016. Batch Process of Polymer-enhanced Ultrafiltration to Recover Mercury (II) from Wastewater. *Journal of Membrane Science.* 514(2016): 229-240.

[10] Van Oers, C. W., Vorstman, M. A. G., Muijselaar, W. G. H. M. and Kerkhof, P. J. A. M., 1992. Unsteady-state Flux Behaviour in Relation to the Presence of a Gel Layer. *Journal of Membrane Science.* 73(2-3): 231-246.

[11] Tuncay, M., Christian, S. D., Tucker, E. E., Taylor, R. W., Scamehorn, J. F. 1994. Ligand-modified Polyelectrolyte-enhanced Ultrafiltration with Electro-static Attachment of Ligands. 1. Removal of Cu(II) and Pb(II) with expulsion of Ca(II). *Langmuir.* 10(12): 4688-4692.

[12] Tuncay, M., Christian, S. D., Tucker, E. E., Taylor, R. W., Scamehorn, J. F. 1994. Ligand-modified Polyelectrolyte-enhanced Ultrafiltration with Electro-static Attachment of Ligands. 2. Use of Diethylenetriaminepentaacetic acid/cations and Polyelectrolyte Mixtures to Remove both Cations and anions from Aqueous Streams. *Langmuir.* 10(12): 4693-4697

[13] Karode, Sandeep K. 2001. Unsteady State Flux Response: A Method to Determine the Nature of the Solute and Gel Layer in Membrane Filtration. *Journal of Membrane Science.* 188(1): 9-20.