

Heavy Metal Removal from Aqueous Solutions by Chitosan Coated Ceramic Membrane

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Abstract A novel method of simultaneous filtration and adsorption of heavy metal using chitosan-coated ceramic membrane is reported. In this study, chitosan was introduced onto the ceramic membrane using a simple dip coating method. Three concentrations of chitosan solution were used, resulting in different amounts of chitosan loadings on the membrane. Scanning electron microscope images showed that the coated chitosan possessed film-like morphology on the membrane surface. The film became thicker and smoother as the chitosan loading increased. These coated membranes were then tested for nickel (Ni) removal at various flow rates. At constant flow rate of 2.5 ml/min and 10, 15 and 20 mg chitosan loadings, the amount of Ni removed were 89.0, 85.1, and 74.2 mg/g chitosan, respectively. When the flow rate was doubled, the amount of Ni removed became 123.0, 113.8, and 100.6 mg/g chitosan, respectively. The amount of Ni removed increased with an increase in flow rate due to larger flow, but decreased with an increase in the amount of chitosan loading, indicating that the adsorption takes place mainly on the surface of chitosan film which, in turn, is controlled by surface area of the membrane. The adsorption kinetics can be well described using the Thomas model.

Keywords: Adsorption; Adsorption kinetics; Ceramic support; Nickel removal; Membrane filtration

1. Introduction

Industrial wastewater remains a major problem in the environment. Toxic heavy metal pollution is one of the most significant environmental problems due to its harmful effects to living organisms and environment [1]. Wastewaters containing heavy metals can cause harmful effects on all forms of life if discharged to the environment without proper treatment [2]. Nickel ions (Ni(II)) is a toxic metal that can cause adverse effects to both human and the environment [3]. Overexposure to Ni(II) ions cause acute effects such as blood and enzyme changes, skin dermatitis, renal edema, diarrhea, and changes in organ iron content [4][5]. Adsorption is also a widely used method that can have quite low cost depending mainly on the sorbent cost. The use of biosorbents has been proposed as an alternative, as it has proven effective on low concentration flows [6]. Membrane technologies can operate with relatively low energy usage [7]. In this investigation an attempt was made to overcome the mass transfer limitations by coating biosorbents, chitosan, on the surface of ceramic membrane. The efficiency for uptake Ni(II) ions onto continuous flow of chitosan coated ceramic membrane was explored. The effect of flow rate and chitosan loading were investigated. Continuous flow adsorption studies were conducted to obtain breakthrough curve and to evaluate the column adsorption performance by using the kinetic model.

2. Materials and Methods

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2.1. Chemicals and Materials

Chitosan was purchased from Bio 21 Co. Ltd, Thailand as a flaked material, with a deacetylation percentage of approximately 85%, size 1-3 mm, and molecular weight of 50,000 daltons. All reagents used were of analytical-reagent grade. A cross-flow microfiltration, ZrO_2 -ceramic tubular membrane (25 mm length, 6 mm internal diameter, 10 mm external diameter, 0.0047 m² effective area, and 0.4 μ m effective pore diameter), were purchased from Tami industries (Germany). Chemicals used in this study consisted of acetic acid (purity 100 %), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, purity 99 %), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were manufactured by Merck. All glassware was washed with 1:1 nitric acid (HNO_3 , purity 65%, Carlo Erba).

2.2. Adsorbent preparation

Chitosan solution (CN) was prepared by dissolving 250, 500 and 1,000 mg chitosan flakes into 250 ml of 1% (v/v) acetic acid solution. The solution was stirred using magnetic stirrer with a mixing speed of 1,200 rpm for 1 h.

2.3. Surface coating of ceramic membrane and characterization

A ceramic membrane was dipped into chitosan solution for 2 min. It was dried at 60 °C in an oven for 15 min. This process is repeated 10 times, and the coated membrane then kept in desiccator before use. The morphology of chitosan coated ceramic membrane was observed by Scanning electron microscope (SEM) (Hitachi Model S-3400N).

2.4. Continuous flow studies

The experiments were carried out in a cross flow filtration as depicted in Fig. 1. The unit includes housing for a single-channel tubular ceramic membrane. The feed tank was filled with a 10 mg/L Ni solution. Permeation and adsorption tests were performed at a gauge pressure of 1 psi. The volumetric flow rates of the feed were controlled by a flow meter at 2.5 and 5.0 ml/min. The effluent samples (feed, retentate and permeate) were collected at pre-determined time. The Ni (II) ions adsorption and water permeation through the CN-coated ceramic membrane were measured. Ni(II) ion concentrations were measured by an atomic absorption spectrometer (Perkin Elmer Analyst 200).

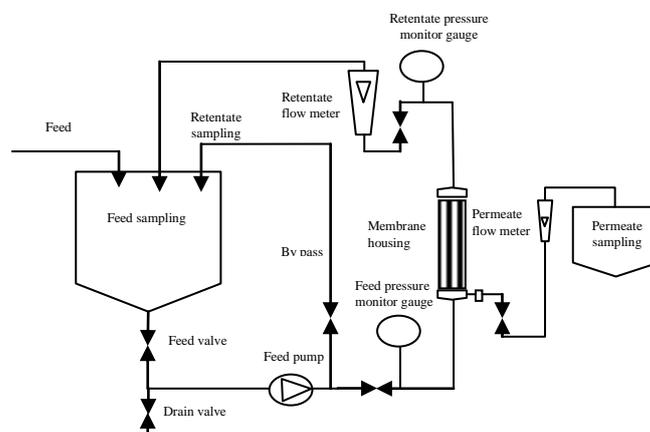


Fig. 1: Experimental setup used for water permeation test and adsorption-microfiltration experiment

The adsorbed amount of Ni(II) ions per unit weight of adsorbent (q_e (mg/g)) was calculated from the mass balance. The adsorption kinetics are applied to the Thomas model and the Yoon-Nelson model equations at various chitosan loading and flow rate.

3. Results and discussion

3.1. Surface coating of ceramic membrane with CN

The SEM images of the uncoated and coated ceramic membranes at three different amounts of chitosan loadings on the surface of ceramic membrane are shown in Fig. 2. From the figure, it is clear that the surface of the ceramic membrane was covered with the CN during the process. In comparison with these four SEM images, the film became thicker and smoother as the chitosan loading increased (Fig. 2b-2d). The SEM pattern of uncoated ceramic membrane shows roughness surface and large pores. The membrane appears to

have less roughness as more chitosan is coated onto the membrane. For 10 mg chitosan loading, the ceramic surface was partially covered by CN solution. Although ceramic surface seems probable a chitosan film covered, it still maintains the membrane. (Fig. 2b). For 15 mg chitosan loading, a thin layer of chitosan can be seen over the top surface. For 20 mg chitosan loading, the surface appears to be covered by a film-like morphology. Due to the chitosan film, Fig. 2c and 2d cannot see membrane particle anymore. With an increase in chitosan loading, the effective pore size of membrane was reduced. These occurred due to the penetration of chitosan molecules into the pores of the membrane [8][9].

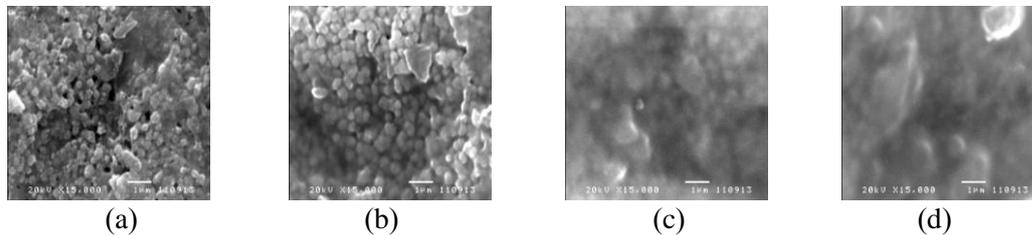


Fig. 2: SEM images of membrane prepared at different amounts of chitosan loadings: (a) 0 mg, (b) 10 mg, (c) 15 mg, and (d) 20 mg.

3.2. Ni(II) ions removal

Removal efficiencies of Ni(II) ions by the method of simultaneous filtration and adsorption is shown in Fig. 3. Ni(II) ions removal up to 76% was accomplished by the CN-coated ceramic membrane with 20 mg chitosan loading at flow rate 2.5 ml/min (Fig. 3a). The specific adsorption capacity (mg Ni/g chitosan) decreased with an increase in chitosan loading. At chitosan loadings of 10, 15 and 20 mg, the specific adsorption capacity was 89.0, 85.1, and 74.2 mg/g chitosan, respectively. When the flow rate was double to 5 ml/min, the specific adsorption capacity was then increased to 123.0, 113.8, and 100.6 mg/g chitosan, respectively (Fig. 3b). At a higher flow rate, more of Ni(II) ions passing through adsorbent, which increased the cumulative adsorption. However, note that the cumulative amount of Ni(II) ions adsorbed increased with an increase in chitosan loading, while the adsorption capacity (amount of Ni/chitosan loading) decreased. This result indicates that the sorption of Ni(II) ions took place primarily on the chitosan surface. When the amount of chitosan coating increased, the surface area also increased but at slower rate due to the change from the particle-like morphology to film-like morphology of chitosan on the membrane support. Although Ni (II) ions adsorption started to level off after 60 min of operation, adsorption approached steady state conditions for Ni(II) ions removal for nearly 240 min of operation (Fig. 3c). It appears that rapid uptake of Ni(II) ions was observed at the beginning of operation and rate decreased thereafter and finally reached saturation.

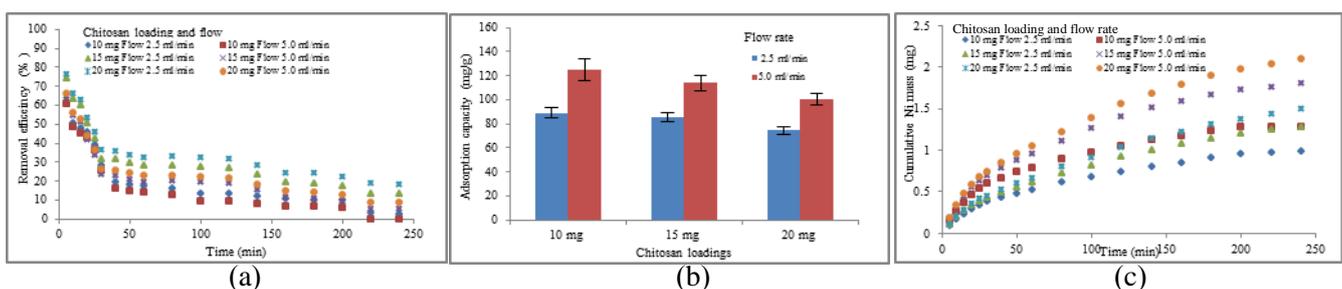


Fig. 3: Adsorption of the Ni(II) ions on CN-coated ceramic membrane at various chitosan loadings and flow rate (a) Time course of Ni(II) ions removal efficiency; (b) adsorption capacity of Ni(II) ions; (c) Time course of the cumulative Ni(II) mass

3.3. Permeate flux

The permeate flux of all conditions decreased with time and leveled off around 100 min. Initially, the permeate flux of all conditions decreased sharply and then the decrease became gradual. Although permeate flux approached steady state conditions for Ni(II) ions removal around 100 min of operation, measurements carried on for 240 min. With an increase in chitosan loadings, the permeate flux decreases because of thicker chitosan layer on membrane surface and the concentration polarization [9]. This tendency showed that interaction between the ceramic membrane and chitosan led to the formation of a chitosan layer on the

membrane ceramic and induced a reduction of the membrane pore size. Membrane compaction and fouling apparently caused a reduction in permeate flux during this period.

3.4. Adsorption kinetics and breakthrough curves

As adsorption and filtration continues, the chitosan-coated membranes gradually become saturated with Ni(II) ions. The plot of C_t/C_0 versus permeate volume as shown in Fig.4 can be used to indicate capacity of this membrane especially when breakthrough of Ni(II) ions in permeate occurs. The breakthrough curves were obtained for the chitosan loadings at 10, 15 and 20 mg with flow rates between 2.5 and 5.0 ml/min. As the chitosan loading on ceramic membrane was increased, the break point time decreased. Decreasing the inflow rate increased the breakthrough volume or breakthrough time. The results also showed that the shape of the breakthrough curve reached saturation (became flat) sooner for a higher chitosan loading. This was because the front of the adsorption zone quickly reached the top of membrane surface [10]. This indicates that the adsorption took place mainly on the chitosan film's surface that is, in turn, controlled by surface area of the membrane. From the shapes of the curves, adsorption may occur in two stages: a rapid rise and a slow rise. The initial rapid rise of breakthrough Ni(II) ions may be due to the saturation of the chitosan active surface across the membrane. After these easily access chitosan sites have been taken, the concentration of the breakthrough Ni(II) ions increases slowly. This may be due to the second slower adsorption of Ni(II) ions by the more difficult to access sites of chitosan, and possibly also to the diffusion of Ni(II) ions already adsorbed on the outer surface of the chitosan film to the inner pores of the chitosan film. For high chitosan loadings of 15 and 20 mg, a turnover point occurred sooner than the 10 mg chitosan loading. A sharp tuning point is an indication that there are likely at least two different adsorption mechanisms involved here.

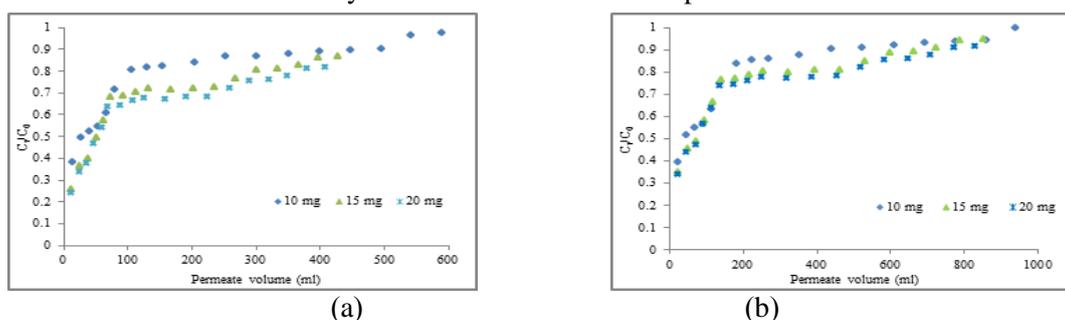


Fig. 4: Influence of chitosan loadings on the breakthrough curve of Ni(II) ions adsorption on CN-coated ceramic membrane (a) flow rate of 2.5 ml/min and (b) flow rate of 5.0 ml/min

Table 1. Characteristic parameters of kinetic model for the adsorption of Ni(II) ions onto CN-coated ceramic membrane

| Chitosan loading | mg | 10.0 | 15.0 | 20.0 | 10.0 | 15.0 | 20.0 |
|-----------------------|-----------|--------|--------|--------|--------|--------|--------|
| Flow rate | ml/min | 2.5 | 2.5 | 2.5 | 5.0 | 5.0 | 5.0 |
| Thomas model | | | | | | | |
| k_{Th} | ml/min mg | 0.0015 | 0.0016 | 0.0008 | 0.0016 | 0.0013 | 0.0011 |
| q_0 | mg/g | 78.10 | 66.39 | 57.39 | 81.79 | 69.62 | 63.59 |
| R^2 | - | 0.974 | 0.933 | 0.889 | 0.969 | 0.985 | 0.976 |
| Yoon and Nelson model | | | | | | | |
| k_{YN} | L/min | 00157 | 0.0112 | 0.0100 | 0.0163 | 0.0116 | 0.0114 |
| τ | min | 13.45 | 48.83 | 63.75 | 0.83 | 19.23 | 14.80 |
| q_{YN} | mg/g | 32.22 | 66.78 | 65.59 | 3.54 | 50.89 | 30.02 |
| R^2 | - | 0.974 | 0.933 | 0.915 | 0.933 | 0.839 | 0.938 |

The adsorption kinetics from these column studies at different chitosan loadings and flow rates were then analyzed using the Thomas and the Yoon–Nelson models [11]. By fitting data using the two models, characteristic parameters for each model were determined and shown in Table 1. The Thomas model provided fit to the experimental data with R^2 values ranging from 0.96 to 0.98 for flow rate 5.0 ml/min and from 0.88 to 0.97 for the flow rate of 2.5 ml/min. The Thomas rate constant (k_{Th}) decreased with an increase in chitosan loading. This indicates that the Ni(II) ions reaction with increasing amount of chitosan is not uniform and the reaction becomes somewhat slower at higher amount of chitosan. The specific adsorption capacity (q_0) decreased as the chitosan loadings increased. With an increase in the flow rate, the specific adsorption capacity also increased because there are more Ni(II) ions flow through. This specific adsorption capacity is also in the same trend as that calculated by using mass balance (section 3.2 above) indicating

applicability of Thomas model in predicting column performance. The Yoon-Nelson model fitting to the data was somewhat less satisfactory compared to that provided by the Thomas model with the R^2 ranging between 0.84-0.94 for the 5 ml/min flow rate, and 0.91-0.97 for the 2.5 ml/min flow rate.

The kinetics study revealed that adsorption of Ni(II) ions onto CN-coated ceramic membrane is better described by the Thomas model rather than the Yoon-Nelson model. Here, the mass transfer limiting mechanism occurred in the first adsorption stage due to surface reaction. The Ni(II) ions adsorption rose rapidly because chitosan active surface was quickly accessed and saturated. In the second slower adsorption stage, the Ni(II) ions already adsorbed on the chitosan surface may slowly diffuse into the inner part of the chitosan film, and hence slowly released the outer sites for further Ni(II) ions adsorption.

4. Conclusions

A novel technique for Ni(II) ions removal from aqueous solution was developed which allowed simultaneous filtration and adsorption using chitosan-coated ceramic membrane. The chitosan-coated membrane in this work has maximum adsorption capacity of 123 mg Ni/ g of coated chitosan, comparable to that of using chitosan nanoparticles but without the difficulty of needing to separate chitosan from treated water. Two Ni adsorption mechanisms were observed from column studies and breakthrough curves, which are the rapid sorption of Ni(II) ions onto chitosan surface followed by the slower intra-particle diffusion of Ni(II) ions inside chitosan structure. Thomas model can also be used to provide good description of the column performance with change in process parameters like chitosan loading and flow rates.

5. Acknowledgements

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6. References

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