High-capacity, nanofiber-based ion-exchange membranes for the selective recovery of heavy metals from impaired waters

Nithinart Chitpong, Scott M. Husson*

Department of Chemical and Biomolecular Engineering and Center for Advanced Engineering Fibers and Films, Clemson University, 127 Earle Hall, Clemson, SC 29634, USA

*Correspondence: shusson@clemson.edu; Tel.: +1 (864) 656-4502; Fax: +1 (864) 656-0784

Abstract

This contribution describes the development, performance evaluation and modeling of polyelectrolyte-modified nanofiber membranes for heavy metal recovery from impaired water. High-capacity membranes were prepared by grafting poly(acrylic acid) (PAA) and poly(itaconic acid) (PIA) to cellulose nanofiber mats. The success of polymer grafting was confirmed by attenuated total reflectance Fourier-transform infrared spectroscopy. Membrane permeabilities for a series of polymer grafted nanofiber membranes were measured by direct-flow filtration. Single-component ion-exchange isotherms were measured at constant pH for cadmium, nickel, and calcium ions. The higher metal-polymer complex stability of Cd-PIA over Cd-PAA was found to be an impact factor for achieving high Cd binding capacities. Single-component ion-exchange isotherms were well described by the Langmuir model, with maximum capacities of PIA-modified membranes that exceeded 220 mg Cd/g, comparable to traditional resin-based ion-exchange media. Moreover, membranes were selective for Cd over Ni and Ca because of different hydration energies and ionization potentials. Competitive ion-exchange measurements were made using environmentally relevant concentrations of these ions to determine the selectivity of the membranes for cadmium ion. Experimental isotherms for Cd-Ca and Cd-Ni were compared to model predictions from the competitive Langmuir model with Langmuir

parameters obtained by fitting single-component isotherms. The competitive Langmuir model well describes the experimental isotherms at low metal ion concentrations. However, at high concentrations, the model underestimates experimental uptake values. This work shows that nanofiber membranes offer a high-capacity and high-productivity platform for selective removal of heavy metals, especially Cd, from impaired waters.

Key words: cadmium, electrospinning, microfiltration, multicomponent ion exchange, polymer grafting

1. Introduction

Heavy metal pollutants are present in wastewaters discharged from metallurgical/metal manufacturing and electroplating facilities, chemical, printing, dye and paint, pulp and paper facilities, textile mills, and petrochemical refineries.¹ This industrial growth in turn, has caused a rise in the heavy metals in wastewater, which has become a global issue of critical environmental importance.¹⁻² Of these toxic metals, cadmium is perhaps the most worrisome, in that it persists in the environment and cannot be broken down into less toxic substances.³⁻⁴ The worldwide production and use of cadmium doubled from 1950 to 1990 and continued to increase especially in Asia until leveling off in 2004 at a value of 2×10^7 kg annually.⁴ Cadmium pollution is particularly concerning in the developing world in that the cadmium waste is not collected separately from general waste, and often ends up in landfills.⁴ The export of new and used products containing cadmium in developing countries that lack the capacity to properly manage and dispose of this lethal metal is also an issue of grave concern, compounded by the fact that only 18% of the global supply of cadmium is recycled.⁴ Nickel is another common toxic

pollutant found in wastewater that can cause great environmental damage.¹

The average cadmium concentrations in industrial wastewater byproducts from electroplating manufacturing facilities fall within a range from 1 to 10 ppm⁵, and the average concentrations of nickel and calcium from industrial effluents released from electroplating and metallurgic industries range from 10 to 40 ppm and 30 to 650 ppm.⁵⁻⁶ Of particular interest to the authors, the United States Environmental Protection Agency (US EPA) has established maximum discharge limits of 0.01 ppm for cadmium and 0.2 ppm for nickel in industrial wastewater effluents; while the Pollution Control Department (PCD), Ministry of Resources and Environment, Thailand has established maximum limits of 0.03 ppm for cadmium and 1.0 ppm for nickel. The control limits are quite low in both the US and Thailand compared to many other countries, particularly those in developing countries, which have much higher limits.⁴

Water purification systems are most important for ensuring that the maximum discharge limits of cadmium and nickel are not exceeded, and many technologies have been developed and evaluated for removal and recovery of such heavy metals from wastewaters.⁷⁻⁸ Among the myriad technologies available, ion-exchange processes with their high treatment capacity, high removal efficiency and rapid kinetics are perhaps the most effective processes for separating specific metal ion impurities from wastewaters.⁸ Key factors determining the cost effectiveness in metal recovery include ion selectivity, which depends on media chemistry, and ion-exchange binding capacity, which closely correlates positively with the surface area. In studies⁹⁻¹¹ to determine the efficacy of ion-exchange membranes for metal ion recovery, high-surface area ion-exchange membranes coated with selective ligands were used to remove cadmium from solution

with higher separation selectivity and volumetric throughput compared to conventional resin-based ion-exchange media.^{8, 10}

Regardless of the separation unit operation, the selective recovery of metals from wastewater is critical particularly when there are differences in toxicity or reuse value. In the case of wastewaters from specific industries, the selectivity of a separation unit operation for a targeted metal ion is important for determining the technical and economic success of the separation process. Many studies undertaken to develop new ion-exchange media evaluate only single-component ion exchange.¹²⁻¹⁴ However, most wastewater effluents from the manufacturing industries listed earlier contain two or more metal ions, making it necessary to study binary- or multicomponent ion exchange to quantify the competing effects of these components for ion exchange sites.

Ion selectivity depends on chemistry. Carboxylate, sulfonate, amino, thiol, amide groups and specialty ligands are examples of functional groups that are useful for capturing metal ions including cadmium and nickel.¹⁵ Polymeric ligands with carboxylate groups have been shown to be effective at complexation with trace heavy metals in industrial wastewaters. Complexing agents such as poly(acrylic acid) (monocarboxylate repeat unit) and succinic acid (dicarboxylate repeat unit) modified cellulose have been useful in recovering such heavy metals as cadmium, copper, nickel, and lead with low power requirements for the recovery process.^{12-14, 16-17}

Additionally, Dowex Retardion 11A8, which is produced by polymerization of acrylic acid within a strong base anion-exchange resin, has been used for the selective capture of cadmium ions in the presence of other heavy metal ions.¹⁸ Dicarboxylate chelating groups (succinic acid

and itaconic acid) also have also been used successfully to develop cadmium binding sorbents with very high binding capacities from 325 mg/g to 405 mg/g.^{13, 17}

The authors describe the efficacy of nanofiber-based ion-exchange membranes in recovering heavy metals such as cadmium and nickel from impaired waters containing one or more metal ions. The objectives were to fabricate membranes with high ion-exchange capacities and to evaluate the membrane selectivity for trace heavy metals in the presence of competing ions. To attain these objectives, macroporous cellulose nanofiber membranes were prepared by electrospinning and modified by grafting polyelectrolytes onto the nanofibers. Electrospinning was used to enhance the volumetric productivity, resulting from high porosity, and binding capacity, which correlates to surface area.¹⁹⁻²² Poly(acrylic acid) (monocarboxyl repeat units) and poly(itaconic acid) (dicarboxyl repeat units) were studied as the polyelectrolyte modifier, as it is possible to improve the ion exchange capacity and selectivity via the chemistry of chelating groups on the grafted polymers. Membrane performance was evaluated by measuring water permeability, metal ion binding capacities, and selectivities. For evaluation of ion-exchange selectivities, binary mixtures of cadmium-nickel and cadmium-calcium were studied. The parameters from fitting single-component ion-exchange isotherms to the Langmuir model were used to predict isotherms in the binary-component systems for comparison to experimental data.

2. Experimental Section

2.1 Materials

The following chemicals were purchased from Sigma-Aldrich (St. Louis, MO) and used as received: azobisisobutyronitrile (AIBN, 98 wt%), cadmium nitrate tetrahydrate

($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), ≥ 99 wt%), cellulose acetate (CA, $M_n = 30,000$ Da by GPC), itaconic acid (IA, ≥ 99 wt%), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ≥ 99.9985 wt%), poly(acrylic acid) (PAA, $M_w = 250,000$ Da, 35 wt% in water), sodium chloride (99 wt%). The following chemicals and solvents were purchased from Fisher Scientific (Waltham, MA): acetone (histological grade), 2-butanol (2-BuOH, 99%), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 95 wt%), dioxane ($\geq 99\%$), and nitric acid (90%, aq). Dimethylacetamide (DMAc, 99 wt%) and sodium hydroxide (pellets, 97 wt%) were purchased from Alfa Aesar (Ward Hill, MA). Chloroform (HPLC grade) was purchased from Honeywell (Morristown, NJ). Poly(glycidyl methacrylate) (PGMA, $M_n = 77,000$ Da) was from the Department of Chemical and Biomolecular Engineering at Clemson University.

2.2 Methods

2.2.1 Preparation of regenerated cellulose nanofiber membrane support

Regenerated cellulose nanofiber membranes were prepared according to the detailed procedure given in a previous publication.²³ Briefly, cellulose acetate in DMAc/acetone solvent was electrospun for 4 h using a voltage of 12.5 kV and a polymer solution flow rate of 0.3 mL/h. Relative humidity of the system was controlled to be higher than 65%RH to avoid bead formation on the fibers. The membranes were **sintered** thermally and converted to regenerated cellulose nanofiber membranes by hydrolysis with 0.1 M NaOH. **Tensile strengths of CA nanofiber membranes before and after the sintering and hydrolysis steps were measured by an ATS 90 tensile tester (Applied Test System Inc., Butler, PA) using the procedures outlined in ASTM D882.** A PGMA solution in chloroform was coated on the regenerated cellulose nanofiber membrane and annealed thermally under vacuum.

2.2.2 Preparation of nanofiber ion-exchange membranes

PIA was prepared by radical polymerization of IA using AIBN as initiator.²⁴ IA (10 g) and dioxane (40 mL) were added into an Erlenmeyer flask (150 mL). Initiator AIBN (0.16 g) was added to the solution containing IA in dioxane, and the mixture was heated for 48 h at 60 °C. Acetone was added to the mixture in a separatory funnel to precipitate PIA overnight. The product PIA ($M_w = 7,000$ Da) was separated from the monomer by vacuum filtration and washed by acetone (50 mL) three times and dried overnight at 50 °C and 50 kPa in a vacuum oven.

The PIA molecular weight was obtained by using the Mark-Houwink-Sakurada relationship given in Eq. 1:

$$[\eta] = KM_v^\alpha \quad (1)$$

$[\eta]$ is intrinsic viscosity, M_v is viscosity average molecular weight, K and α are constants for a particular polymer-solvent pair at a particular temperature. Since constants K and α were not available from the literature for PIA, they were approximated by measurements using standards of PAA (which has similar molecular structure). A glass capillary viscometer (Model: 1-1598, Cannon Instrument Co., State College, PA) was used to measure the intrinsic viscosities of deprotonated PAA standard ($M_w = 100,000$ Da and 250,000 Da) solutions at concentrations of 1 wt% and 0.5 wt% in DI water. These data were used to determine the constants in Eq. 1. Intrinsic viscosities of PIA solutions at concentrations of 1 wt% and 0.5 wt% were measured and the molecular weight was calculated from Eq. 1 using K and α obtained from PAA measurements.

PAA and PIA were dissolved in water to prepare 7 wt% solutions. All polymer solutions were sonicated for 1 h or until they formed a homogenous solution. Each polymer solution was passed through a cellulose acetate sterile syringe filter (pore size 0.45 μm) purchased from VWR International (Radnor, PA) to remove large size aggregates before use. Each PGMA-functionalized nanofiber membrane was submerged in 4 mL of the filtered polymer solution for 5 min, removed from solution and annealed at 70 °C for 2 h. Thereafter, the membranes were washed three times (5 min per wash step) by immersing in 30 mL of water to remove any non-grafted polymer. Scheme S1 (supplementary materials) illustrates the reaction between PAA or PIA and PGMA.

2.3 Characterization

2.3.1 Surface morphology

The uniformity, quality and average diameter of fibers were examined by optical microscopy at 10X magnification (model: B100-B, Amscope, Irvine, CA) and scanning electron microscopy (SEM model: S4800, Hitachi High Technologies America, Inc., Schaumburg, IL).

Representative 0.5 cm^2 samples of the membranes were attached with carbon tape to aluminum stubs prior to the SEM measurements. The SEM measurements were performed at an accelerating voltage of 5.0 kV, current of 2 mA and magnifications of 3000x, 6000x and 12000x.

2.3.2 Nanofiber membrane physical properties

Average thicknesses of the water-wet nanofiber membranes were measured at five different spots on the membrane using a digital micrometer (model ME-50HA) with flat probe tips and ceramic stand (model MS-11C) from Nikon Metrology Inc. (Brighton, MI).

The fluid displacement method using 2-butanol was used to measure membrane porosities, ϵ , defined as the quotient of the pore volume to the total volume of the porous membrane. Details of this measurement were provided in a previous publication.²³

2.3.3 Surface chemistry

Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) analyses were performed using a Thermo Scientific Nicolet Nexus 870-IR spectrometer and Omnic version 8.3 software. All measurements used an automatic signal gain, 32 scans and 4.0 cm^{-1} resolution. The background was scanned after each measurement. An ATR correction was applied, and baselines were manually corrected consistently for all spectra.

2.4 Performance properties of nanofiber membranes

2.4.1 Direct-flow water flux measurements

Each membrane sample was cut to 45 mm diameter using a circular die and placed into a 50 mL ultrafiltration stirred cell (Amicon Model 8050, EMD Millipore, Billerica, MA). DI water was supplied continuously to the ultrafiltration cell from a 3.78 L storage tank connected to an air cylinder. Flux measurements were made at constant pressures from 20.7 to 62.0 kPa, which were measured by a pressure transducer (Series 100, Transmetrics, Solon, OH). The filtrate mass and filtration time were recorded to calculate the flux and permeability. Three measurements at each pressure were made in order of increasing pressure, and then repeated in order of decreasing pressure to check whether membrane compaction occurred at the higher pressures. Flux data are reported as averages of the measurements at each pressure, applying a correction for the system

resistance.

2.4.2 Static binding capacity measurements

Cadmium, nickel and calcium solutions with concentrations from 5 to 200 mg/L in DI water were prepared from $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. Mixed ion solutions were prepared comprising Cd(II) at concentrations of 5 and 10 mg/L and Ni(II) at concentrations of 20 and 40 mg/L, as well as Cd(II) at concentrations of 5 and 10 mg/L and Ca(II) at concentrations of 100, 300, and 500 mg/L. PAA-modified nanofiber membranes and PIA-modified nanofiber membranes were neutralized by sodium hydroxide solution (0.05M) for 1 h and dried by a stream of N_2 gas. Afterwards, membranes were cut into small pieces, weighed and contacted with the metal ion solutions (3 mL) for at least 15 h with stirring, which previously was confirmed by kinetic studies to be sufficient time to reach equilibrium.²³

Inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer, Optima 5300 DV) was used to measure Cd(II), Ni(II) and Ca(II) concentrations. The peak area for each ion was measured five times for each sample and the calibration solutions. Reported values are given with uncertainties that represent one standard deviation between the average values for at least two samples.

3. Results and Discussion

3.1 Characterization of nanofiber membrane

3.1.1 Membrane surface chemistry

Scheme S1 (see supplementary materials) illustrates the reaction between PGMA and

regenerated cellulose. A fraction of the epoxy functional groups of PGMA react with hydroxyl groups of regenerated cellulose. Residual epoxy groups are available to react with carboxyl groups of PAA and PIA. Reactions of glycidyl methacrylate with hydroxyl and carboxylic groups occurs through an epoxide ring-opening pathway.²⁵ The mechanism begins with the transfer of a proton from hydroxyl or carboxyl groups to an epoxide group of PGMA to form a strong electrophile.²⁵⁻²⁶ When the PGMA reacts with the hydroxyl group of RC or carboxyl group of PAA or PIA, lone pair electrons of the oxygen undergo nucleophilic attack of a carbon in the epoxide ring.²⁵ As a result, an epoxide ring-opening reaction occurs to yield an ether or ester product for the reaction with RC and with PAA or PIA, respectively.²⁵⁻²⁶ Spectrum B in Fig. 1 shows clear evidence of carbonyl group stretching of PGMA at 1730 cm^{-1} that was not observed in spectrum A of regenerated cellulose. Spectra C and D in Fig. 1 show evidence for carboxylic acid group stretching of PAA and PIA at 1705 cm^{-1} . Additionally, the broad peak assigned to OH stretching in cellulose at over 3000 cm^{-1} decreased slightly following PGMA grafting and increased significantly after PAA and PIA grafting by OH stretching from carboxyl groups.²⁷

PAA and PIA grafting densities were determined using a procedure described previously.²³ Grafting densities were $0.027 \pm 0.008\text{ chains/nm}^2$ and $0.64 \pm 0.28\text{ chains/nm}^2$ for PAA- and PIA-modified membranes. Based on these grafting densities and the molar masses of the polymers, the areal densities of carboxyl groups are roughly $90 \pm 27\text{ groups/nm}^2$ and $69 \pm 39\text{ groups/nm}^2$ for PAA- and PIA- modified membranes. The uncertainty represents one standard deviation among five samples. Since it is not possible to know with certainty the actual polymer chain architecture on the membrane pore surfaces, we estimated the chain density per surface area of

membranes assuming close-packed chains (onset of polymer brush regime), anchored at one point with projected areas based on the radius of gyration (R_g) in solution from Eq. 2:

$$R_g = a(N/6)^{0.5} \quad (2)$$

N is the degree of polymerization and a is the statistical segment ($a = 0.65$ nm was used for PAA and approximately used for PIA). Calculated R_g for PAA and PIA molecular weights of 250,000 and 7,000 g/mol were 15.6 and 2.0 nm, respectively. Therefore, the ratio of projection areas of PAA and PIA chains is approximately 1:61 resulting in an expected chain density of PIA to be about 61 times higher than that for PAA. Based on this estimated ratio of chain densities and the molecular weights of PAA and PIA used, the number of carboxyl groups of PIA (dicarboxylate repeat unit) should be 1.9 times higher than PAA (monocarboxylate repeat unit). However, experimentally, it was found that the areal densities of carboxyl groups of PAA and PIA are similar. It was reported that polymers with higher molecular weight tend to have slow diffusion of entangled chains preventing reaction of end-functional groups of the polymer chains with epoxy groups of PGMA.²⁸ Therefore, the high molecular weight PAA used in this study may have relatively fewer attachments to PGMA than the low molecular weight PIA, resulting in a higher number of available carboxyl groups. Furthermore, polymers with lower molecular weight penetrate extensively into the PGMA anchoring layers.²⁸ In the case of PIA, significant interpenetration into PGMA may lead to an even greater extent of multipoint anchoring than occurs with the high molecular weight PAA, resulting in a significantly lower ratio of grafting densities than is calculated based on the assumption of close-packed chains anchored at one point. This might explain our experimental results that the carboxyl group densities of PAA and PIA are not statistically different at 68% confidence levels.

3.1.2 Surface morphology

Fig. 2A provides representative SEM images showing the surface morphology of regenerated cellulose nanofibers before surface modification. The RC electrospun fibers have diameters in the submicron range (200 - 500 nm). Rough surfaces of individual regenerated cellulose nanofibers appear after modification with PGMA (in chloroform), as shown in Fig. 2B. Finally, Fig. 2C and 2D show fibers coated with PAA and PIA. The PAA and PIA thin films coat the surfaces of individual nanofibers and partially fill the pore spaces among nanofibers, causing an observed decrease in porosity.

3.1.3 Nanofiber membrane physical properties

Table 1 summarizes the physical properties of nanofiber membranes. Average thicknesses were measured at five different spots on each membrane sample to evaluate uniformity. Thicknesses increased on average after grafting PAA and PIA, but the increase was not statistically significant at one standard deviation. The porosities were measured by liquid displacement using 2-butanol as the displacement fluid because it does not swell the membranes based on thickness measurements, and because it has a slow evaporation rate. It was discovered that PAA and PIA grafting reduced the nanofiber membrane porosity by 15-20%. This result is consistent with SEM images in Fig. 2 that show pore constriction by the thin film coating of each polymer grafted to nanofiber membranes.

3.2 Membrane performance properties

3.2.1 Permeability studies

Flux measurement experiments enable the comparison of the pure water permeabilities of

nanofiber membranes before and after modification with PAA and PIA. Fig. 3 demonstrates that the permeabilities of PAA and PIA modified nanofiber membranes decreased by about 85% relative to PGMA-coated nanofiber membranes. The Kozeny-Carman equation (Eq. 3) was used to model the permeability data.

$$\mathcal{P} = \frac{k\varepsilon^3}{L(1-\varepsilon)^2} \quad (3)$$

?? represents permeability (L/m²/bar/h), L represents membrane thickness and ε represents membrane porosity. Experimental permeability, thickness and porosity data (Table 1) for unmodified RC nanofiber membranes were used to find the proportionality constant, k. Eq. 3 then was used to predict permeabilities for membranes modified by PGMA-PAA and PGMA-PIA according to the measured thicknesses and porosities reported in Table 1. Similarly to previous work with PAA²³, the model overestimates experimental permeabilities due to polymer swelling during flux measurement experiments with water, which is a better solvent than the 2-butanol used to determine porosity values.

For comparison, a commercial regenerated cellulose microfiltration membrane (Whatman RC 60) with the same nominal pore diameter as the nanofiber membranes (ca. 1 μ m) was modified with 250K PAA. The permeability (4800 $\pm$ 300 LMH/bar) was higher than the PAA modified nanofiber membranes; however, the maximum Cd capacity of the nanofiber membrane was measured to be 1.79 times higher than the RC 60 membrane (vide infra). Such tradeoffs between capacity and permeability are common.

3.2.2 Cd(II), Ni(II) and Ca(II) static binding capacity

3.2.2.1 Single-component ion exchange for Cd(II), Ni(II) and Ca(II) on PAA and PIA

modified nanofiber membranes

To create highly permeable, ion-selective membranes with high sorption capacity, polyacid-functionalized nanofiber membranes were produced and evaluated firstly for single-component static (i.e., equilibrium) ion exchange with Cd(II), Ni(II) and Ca(II) at $25 \pm 2^\circ\text{C}$. Industrial wastes containing cadmium often contain nickel. In addition, calcium is a common divalent ion found in environmental waters. Fig. 4 and 5 compare the ion-exchange isotherms of Cd(II), Ni(II) and Ca(II) on PAA modified nanofiber membranes. The PAA modified nanofiber membranes are selective for Cd(II) over Ni(II) and Ca(II) according to the maximum ion-exchange capacities in Table 2. PIA modified nanofiber membranes were prepared to compare the membrane performance to PAA modified membranes. Dicarboxylate groups have been found to bind metal ions through chelation with higher binding capacity than monocarboxylate groups because of higher complex stabilities.^{13, 29-30} Similarly to PAA modified membranes, Fig. 5 and Table 2 show that PIA modified membranes are selective for Cd(II) over Ni(II) and Ca(II). However, equilibrium uptake per unit mass of polymer (PAA or PIA) or per number of carboxyl groups might be more effective to compare the ligand-metal binding. Table S1 (see supplementary materials) reports that the metal binding capacities (mmol of metal per g of polymer and mmol of metal per carboxyl group) of Cd(II), Ni(II) and Ca(II) on PAA and PIA modified nanofiber membranes are not different at 68% confidence level. **Additionally, Table 3 demonstrates that PAA and PIA modified membranes had high Cd binding capacities and these capacities are competitive to commercial ion-exchange resins and higher than other functionalized microfiltration membranes.**

Statistically, there was no difference between binding capacities on a per carboxylate group

basis; however, there does appear to be a 62% and 71% higher average binding capacity for Cd(II) on the PIA modified membrane than for Ni(II) or Ca(II). This result can be explained partially on the basis of ion hydration. The Gibbs energy of hydration is less negative for Cd(II) (-1780 kJ/mol) than Ni(II) (-2050 kJ/mol), largely due to the hydration enthalpy of nickel ions (-2138 kJ/mol) being more negative than that of cadmium ions (-1837 kJ/mol).³¹⁻³² Therefore, nickel ions experience a higher degree of water shielding and, thus, hydrated nickel ions present a lower effective charge than hydrated cadmium ions in solution.³¹ Thus, complex formation with the ligand is more stable with cadmium than with nickel ions as shown in the literature.²⁹ Calcium, on the other hand, has lower binding capacity than either nickel or cadmium despite having a less negative Gibbs energy of hydration (-1560 kJ/mol). However, it was reported in the literature³³ that the complex stability (i.e., interaction affinity) of Cd-oxygen donor groups is higher than that for Ca-oxygen donors according to Irving-Williams concept³⁴, which proposes that metal-ligand complex stability is affected not only by the hydration energy but also by the ionic radii and total ionization potential of metal ions.³⁴ Replacing water molecules in the hydration complex of small metal cations by larger ligand groups decreases electrostatic interaction due to the greater charge separation. This effect is more significant for Ni(II) ions (0.73 Å) than larger Cd(II) ions (0.96 Å) (the gain in covalent interaction energy is much the same due to similar ionization potential ~ 2500 kJ/mol).³⁴ On the other hand, larger Ca(II) ions (0.99 Å) with low ionization potential (~ 1750 kJ/mol) have lower complex stability compared with Cd(II) (which has the higher ionization potential).³⁴ Also, it has been reported that calcium ions have lower affinity for complexation with carboxylic acids than cadmium ions.³⁵ Additionally, the higher average binding capacity for Cd(II) over Ni(II) might be explained by a lower strain energy on a seven-membered ring of cadmium-IA complex (one metal coordinated

to two carboxylate anions in one polymer repeat unit) resulting higher complex stability. As stated in the literature³⁶⁻³⁷, metal ion size and the metal-IA ring size effect complex stability, and larger metal ions Cd(II) (ionic radius of 0.97 Å) would experience a low strain energy, while small metal ion Ni(II) (ionic radius of 0.69 Å) would experience a high strain energy, and hence a lower complex stability.

Since the membranes were functionalized by polymers with one type of functional group (either monocarboxylate for PAA or dicarboxylate for PIA), all ion-exchange sites were assumed to be identical for a given membrane type. By further assuming monolayer site coverage, experimental data were fitted to the Langmuir isotherm model (Eq. 4) to evaluate the apparent (i.e., based on concentration) metal ion association coefficient (K_i) and maximum metal ion-exchange capacities ($Q_{max,i}$). Table 2 summarizes the results. Symbols in Figures 4 and 5 represent experimental data and curves represent fits to the Langmuir isotherm model. While the mechanism for binding really is ion exchange, the Langmuir isotherm works well because the system has a constant pH.

$$\frac{Q_i}{Q_{max,i}} = \frac{K_i C_{e,i}}{1 + K_i C_{e,i}} \quad (4)$$

Q_i is the equilibrium uptake of ion i per unit mass of membrane, and $C_{e,i}$ is the equilibrium concentration of ion i in solution. Here capacities are reported on a mass (or volume) of membrane basis. From an engineering standpoint, defining capacity in this way makes more sense since the footprint of the unit operation will be based on the unit volume of the membrane column, which incorporates both the support membrane and the functional polymer coating.

3.2.2.1 Binary-component ion exchange for Cd(II), Ni(II) and Ca(II) on PAA and PIA

modified nanofiber membranes

Cd-Ni and Cd-Ca binary systems were studied to quantify the competitive ion-exchange effects. Experimentally, mixture solutions of Cd (II) and Ni(II) and mixture solutions of Cd(II) and Ca(II) were prepared in the range of ion concentrations found typically in actual wastewater and specifically with concentrations given in Table 4. The equilibrium concentrations of metal ions before and after ion exchange on PAA- and PIA-modified membranes were measured by ICP-OES and used to calculate the equilibrium capacities by mass balance. Results of the equilibrium measurements in Table 4 are reported with uncertainties that represent one standard deviation between two membrane samples. Additionally, to evaluate the ability of the model to represent the experimental data, equilibrium concentrations from experiments were used to calculate predicted equilibrium uptake values using the competitive Langmuir model in Eq. 5 using constants derived from fits to the single-component isotherms. Table 4 presents the results.

$$\frac{Q_i}{Q_{max,i}} = \frac{K_i C_{e,i}}{1 + \sum_{j=1}^N K_j C_{e,j}} \quad (5)$$

In Cd-Ni system modeling, initial concentrations of each component were varied from 0.0 to 40.0 mg/L as shown in Tables S2 and S3 (see supplementary material). Similarly, the Cd-Ca system was modeled with initial concentrations of each component from 0.0 to 500.0 mg/L as shown in Tables S4 and S5 (see supplementary material). The model-derived uptake values for the Cd-Ni system for PAA and PIA- modified membranes are displayed as 2D plots in Fig. 6 and 3D surface plots in Figs. 7 and 8. The experimental data in Table 4 were included in the 3D plots as symbols. To visualize more clearly, Figs. 9 and 10 illustrate the comparison between prediction values and experimental data for the Cd-Ni system with uncertainties that represent one standard deviation between two membrane samples. The predictions generally are satisfactory and within the range of uncertainties of experimental data at the 99% confidence

level. However, the experimental capacity data in the Cd-Ca system are higher than the model predicted values as shown in Table 4 and in the 2D and 3D plots (Figures S3-S6 in supplementary material) for both PAA and PIA-modified membranes. In some situations, the Langmuir model might well describe the experimental uptake isotherm at low uptake values and deviate at high uptake values due to cooperative interactions among bound ions. Thus, we considered these cooperative interactions among ions in the binary system by including them in the model. Equation 5 shows the competitive Langmuir model for a binary-component system that includes parameters (E_{ii} , E_{ij} , E_{ij}) to account for interactions between ions i and j :³⁸

$$\frac{Q_i}{Q_{max,i}} = \frac{K_i C_{e,i} + \frac{1}{2} K_i^2 E_{ii}^2 + \frac{1}{2} K_i K_j E_{ij} C_{e,i} C_{e,j}}{1 + K_i C_{e,i} + K_j C_{e,j} + \frac{1}{4} K_i^2 E_{ii} C_{e,i}^2 + \frac{1}{4} K_j^2 E_{jj} C_{e,j}^2 + \frac{1}{2} K_i K_j E_{ij} C_{e,i} C_{e,j}} \quad (6)$$

$E_{ij} = \exp(-W_{ij}/kT)$ and W_{ij} is the interaction energy between ions i and j . Values for W_{ii} and W_{jj} were obtained from fits to single-component isotherms, and a value for W_{ij} was estimated using a geometric mean combining rule: $W_{ij} = \sqrt{W_{ii} W_{jj}}$.³⁸ Although this model was fitted to the experiment data, it was not able to describe the deviations between experimental and model data at high uptake values. It therefore remains unclear what is the cause for this deviation.

Conclusions

Poly(acrylic acid) and poly(itaconic acid) modified electrospun cellulose nanofiber membranes offer a high productivity platform for selective removal of heavy metals, especially Cd, from impaired water. The type of grafted polymer plays a role in the membrane ion-exchange performance, with dicarboxylate groups showing higher selectivity for cadmium over competing divalent ions. Unlike membrane unit operations such as reverse osmosis and nanofiltration that operate based on ion rejection, these ion-exchange membranes provide the opportunity to remove specific, trace metal ions by selective interaction between membrane functional groups

and the metal ions. This ion selectivity is important when there are differences in toxicity or reuse value. Ongoing work is evaluating the dynamic binding capacities for these new membranes.

Acknowledgements

Funding for this work was provided by the Department of Chemical and Biomolecular Engineering, Clemson University; the Office of the Civil Service Commission (OCSC), Thailand; and the Ministry of Science and Technology (MOST), Thailand. We thank Kimberly Ivey of the Clemson University Department of Materials Science and Engineering for assistance using ATR-FTIR equipment. We thank Dr. Konstantin Kornev and Dr. Chen-Chih Tsai for assisting with the design of the electrospinning equipment and methods development. We thank Dr. Amod A. Ogale and Ozgun Ozdemir for providing access to and assistance with the hydraulic hot press equipment. We thank Dr. Igor Luzinov for advice on graft modification strategies. We thank for Dr. Brian Powell, Kayla Collins and Anne Cummings for providing access to and assistance with ICP-OES equipment. We thank Dr. Zhou Jinxiang for supplying PGMA.

References

Uncategorized References

1. Srivastava, V. C.; Mall, I. D.; Mishra, I. M., Competitive adsorption of cadmium (II) and nickel (II) metal ions from aqueous solution onto rice husk ash. *Chemical Engineering and Processing: Process Intensification* **2009**, 48 (1), 370-379.
2. Nakate, S. Three major types of environmental pollution. Available online: <http://www.buzzle.com/articles/three-major-types-of-environmental-pollution.html> (Accessed on 01.05.14).
3. Exposure to cadmium: A major public health concern. World health organization 2010: the WHO Document Production Services, Geneva, Switzerland, 2010.
4. Final review of scientific information on cadmium, United nations environment programme (UNEP), Chemicals branch: DTIE, Nairobi, Kenya 2010.
5. Chaiyasith, S.; Chaiyasith, P.; Septhum, C., Removal of cadmium and nickel from aqueous solution by adsorption onto treated fly ash from Thailand. *Thammasat International Journal of Science and Technology* **2006**, 11 (2).
6. Maine, M.; Sune, N.; Hadad, H.; Sánchez, G.; Bonetto, C., Nutrient and metal removal in a constructed wetland for wastewater treatment from a metallurgic industry. *Ecological Engineering* **2006**, 26 (4), 341-347.
7. Barakat, M., New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry* **2011**, 4 (4), 361-377.

8. Fu, F.; Wang, Q., Removal of heavy metal ions from wastewaters: a review. *Journal of Environmental Management* **2011**, 92 (3), 407-418.
9. Zhang, L.; Zhou, J.; Zhou, D.; Tang, Y., Adsorption of cadmium and strontium on cellulose/alginic acid ion-exchange membrane. *Journal of Membrane Science* **1999**, 162 (1), 103-109.
10. Zhang, L.; Zhao, Y.-H.; Bai, R., Development of a multifunctional membrane for chromatic warning and enhanced adsorptive removal of heavy metal ions: application to cadmium. *Journal of Membrane Science* **2011**, 379 (1), 69-79.
11. Xu, T., Ion exchange membranes: state of their development and perspective. *Journal of Membrane Science* **2005**, 263 (1), 1-29.
12. Okieimen, F.; Sogbaike, C.; Ebhoaye, J., Removal of cadmium and copper ions from aqueous solution with cellulose graft copolymers. *Separation and Purification Technology* **2005**, 44 (1), 85-89.
13. Stephen, M.; Catherine, N.; Brenda, M.; Andrew, K.; Leslie, P.; Corrine, G., Oxolane-2, 5-dione modified electrospun cellulose nanofibers for heavy metals adsorption. *Journal of Hazardous Materials* **2011**, 192 (2), 922-927.
14. Geay, M.; Marchetti, V.; Clément, A.; Loubinoux, B.; Gérardin, P., Decontamination of synthetic solutions containing heavy metals using chemically modified sawdusts bearing polyacrylic acid chains. *Journal of Wood Science* **2000**, 46 (4), 331-333.
15. Ma, H.; Hsiao, B. S.; Chu, B., Electrospun nanofibrous membrane for heavy metal ion adsorption. *Current Organic Chemistry* **2013**, 17 (13), 1361-1370.

16. Güçlü, G.; Gürdağ, G.; Özgümüş, S., Competitive removal of heavy metal ions by cellulose graft copolymers. *Journal of Applied Polymer Science* **2003**, 90 (8), 2034-2039.
17. Kyzas, G. Z.; Siafaka, P. I.; Lambropoulou, D. A.; Lazaridis, N. K.; Bikiaris, D. N., Poly (itaconic acid)-grafted chitosan adsorbents with different cross-linking for Pb (II) and Cd (II) uptake. *Langmuir* **2014**, 30 (1), 120-131.
18. Samczyński, Z.; Dybczyński, R., Some examples of the use of amphoteric ion-exchange resins for inorganic separations. *Journal of Chromatography A* **1997**, 789 (1), 157-167.
19. Haider, S.; Park, S.-Y., Preparation of the electrospun chitosan nanofibers and their applications to the adsorption of Cu (II) and Pb (II) ions from an aqueous solution. *Journal of Membrane Science* **2009**, 328 (1), 90-96.
20. Callegari, G.; Tyomkin, I.; Kornev, K. G.; Neimark, A. V.; Hsieh, Y.-L., Absorption and transport properties of ultra-fine cellulose webs. *Journal of Colloid and Interface Science* **2011**, 353 (1), 290-293.
21. Saeed, K.; Haider, S.; Oh, T.-J.; Park, S.-Y., Preparation of amidoxime-modified polyacrylonitrile (PAN-oxime) nanofibers and their applications to metal ions adsorption. *Journal of Membrane Science* **2008**, 322 (2), 400-405.
22. Ramakrishna, S.; Fujihara, K.; Teo, W.-E.; Yong, T.; Ma, Z.; Ramaseshan, R., Electrospun nanofibers: solving global issues. *Materials Today* **2006**, 9 (3), 40-50.

23. Chitpong, N.; Husson, S. M., Polyacid functionalized cellulose nanofiber membranes for removal of heavy metals from impaired waters. *Journal of Membrane Science* **2017**, *523*, 418-429.
24. Stawski, D.; Polowinski, S., Polymerization of itaconic acid. *Polimery* **2005**, *50* (2), 118-122.
25. Reis, A. V.; Fajardo, A. R.; Schuquel, I. T.; Guilherme, M. R.; Vidotti, G. J.; Rubira, A. F.; Muniz, E. C., Reaction of glycidyl methacrylate at the hydroxyl and carboxylic groups of poly (vinyl alcohol) and poly (acrylic acid): is this reaction mechanism still unclear? *The Journal of Organic Chemistry* **2009**, *74* (10), 3750-3757.
26. Wade, L. G.; Simek, J. W., *Organic chemistry*. Pearson Higher Ed: Upper Sanddle, NJ, 2016.
27. Dong, J.; Ozaki, Y.; Nakashima, K., Infrared, Raman, and near-infrared spectroscopic evidence for the coexistence of various hydrogen-bond forms in poly (acrylic acid). *Macromolecules* **1997**, *30* (4), 1111-1117.
28. Iyer, K. S.; Luzinov, I., Effect of macromolecular anchoring layer thickness and molecular weight on polymer grafting. *Macromolecules* **2004**, *37* (25), 9538-9545.
29. Yasuda, M.; Yamasaki, K.; Ohtaki, H., Stability of complexes of several carboxylic acids formed with bivalent metals. *Bulletin of the Chemical Society of Japan* **1960**, *33* (8), 1067-1070.
30. O'Connell, D. W.; Birkinshaw, C.; O'Dwyer, T. F., Heavy metal adsorbents prepared from the modification of cellulose: A review. *Bioresource Technology* **2008**, *99* (15), 6709-6724.

31. Salehi, E.; Madaeni, S.; Heidary, F., Dynamic adsorption of Ni (II) and Cd (II) ions from water using 8-hydroxyquinoline ligand immobilized PVDF membrane: Isotherms, thermodynamics and kinetics. *Separation and Purification Technology* **2012**, *94*, 1-8.
32. Wright, D.; Holloway, J.; Reilley, C., Heat and entropies of formation of metal chelates of polyamine and polyaminocarboxylate ligands. *Analytical Chemistry* **1965**, *37* (7), 884-892.
33. Dronnet, V.; Renard, C.; Axelos, M.; Thibault, J.-F., Characterisation and selectivity of divalent metal ions binding by citrus and sugar-beet pectins. *Carbohydrate Polymers* **1996**, *30* (4), 253-263.
34. Irving, H.; Williams, R., 637. The stability of transition-metal complexes. *Journal of the Chemical Society (Resumed)* **1953**, 3192-3210.
35. Benedetti, M. F.; Milne, C. J.; Kinniburgh, D. G.; Van Riemsdijk, W. H.; Koopal, L. K., Metal ion binding to humic substances: application of the non-ideal competitive adsorption model. *Environmental Science & Technology* **1995**, *29* (2), 446-457.
36. Hancock, R. D., Chelate ring size and metal ion selection. The basis of selectivity for metal ions in open-chain ligands and macrocycles. *Journal of Chemical Education* **1992**, *69* (8), 615.
37. Cukrowski, I.; Marsicano, F.; Hancock, R. D.; Tshetlho, P. T.; Van Otterlo, W. A., The neutral oxygen donor in complexes of lead and cadmium: A differential pulse polarographic, potentiometric and calorimetric study. *Polyhedron* **1995**, *14* (12), 1661-1674.
38. Hill, T. L., *An introduction to statistical thermodynamics, Chapter 7*. Dover Publications, Inc.: Newyork, 1986.

39. Pehlivan, E.; Altun, T., The study of various parameters affecting the ion exchange of Cu ²⁺, Zn ²⁺, Ni ²⁺, Cd ²⁺, and Pb ²⁺ from aqueous solution on Dowex 50W synthetic resin. *Journal of Hazardous Materials* **2006**, *134* (1), 149-156.
40. Kumar, U., Agricultural products and by-products as a low cost adsorbent for heavy metal removal from water and wastewater: A review. *Scientific Research and Essays* **2006**, *1* (2), 033-037.
41. Shibi, I. G.; Anirudhan, T. S., Polymer- grafted banana (*Musa paradisiaca*) stalk as an adsorbent for the removal of lead (II) and cadmium (II) ions from aqueous solutions: kinetic and equilibrium studies. *Journal of Chemical Technology and Biotechnology* **2006**, *81* (3), 433-444.
42. Wei, W.; Kim, S.; Song, M.-H.; Bediako, J. K.; Yun, Y.-S., Carboxymethyl cellulose fiber as a fast binding and biodegradable adsorbent of heavy metals. *Journal of the Taiwan Institute of Chemical Engineers* **2015**, *57*, 104-110.
43. Tay, C.-C.; Liew, H.-H.; Redzwan, G.; Yong, S.-K.; Surif, S.; Abdul-Talib, S., *Pleurotus ostreatus* spent mushroom compost as green biosorbent for nickel (II) biosorption. *Water Science and Technology* **2011**, *64* (12), 2425-2432.
44. Swelam, A.; El-Nawawy, M.; Salem, A.; Ayman, A., Evaluation of Amberjet 1500H, Amberjet 1300H and Amberlite IRC 86 Ion-Exchange Resins for the Removal of Toxic Nickel Ions from Aqueous Solution.
45. Malla, M. E.; Alvarez, M. B.; Batistoni, D. A., Evaluation of sorption and desorption characteristics of cadmium, lead and zinc on Amberlite IRC-718 iminodiacetate chelating ion exchanger. *Talanta* **2002**, *57* (2), 277-287.

46. ChamCarthy, S.; Seo, C. W.; Marshall, W. E., Adsorption of selected toxic metals by modified peanut shells. *Journal of Chemical Technology and Biotechnology* **2001**, 76 (6), 593-597.
47. Kara, A.; Acemioğlu, B.; Alma, M. H.; Cebe, M., Adsorption of Cr (III), Ni (II), Zn (II), Co (II) ions onto phenolated wood resin. *Journal of applied polymer science* **2006**, 101 (5), 2838-2846.
48. Yu, Z.; Qi, T.; Qu, J.; Wang, L.; Chu, J., Removal of Ca (II) and Mg (II) from potassium chromate solution on Amberlite IRC 748 synthetic resin by ion exchange. *Journal of hazardous materials* **2009**, 167 (1), 406-412.
49. Ritchie, S.; Bachas, L.; Olin, T.; Sikdar, S.; Bhattacharyya, D., Surface modification of silica-and cellulose-based microfiltration membranes with functional polyamino acids for heavy metal sorption. *Langmuir* **1999**, 15 (19), 6346-6357.

Table 1. Impact of polymer grafting on nanofiber membrane properties

Nanofiber membrane	Thickness		Porosity	
	μm	SD	%	SD
Before polymer grafting	74	17	77	3.5
After PAA grafting	81	8.3	60	0.3
After PIA grafting	82	6.5	62	3.1

Table 2. Summary of Langmuir isotherm constants for Cd(II), Ni(II) and Ca(II) on PAA and PIA modified electrospun cellulose nanofiber membranes

Sorbent material	Binding ion	Maximum ion-exchange capacity, $Q_{\max}$ (mg/g)	Apparent association coefficient, K (mL/mg)
RC-PGMA-PAA	Cd(II)	162	4.6×10^{-2}
RC-PGMA-PAA	Ni(II)	107	2.5×10^{-2}
RC-PGMA-PAA	Ca(II)	85	8.5×10^{-3}
RC-PGMA-PIA	Cd(II)	222	1.5×10^{-1}
RC-PGMA-PIA	Ni(II)	52	1.4×10^{-1}
RC-PGMA-PIA	Ca(II)	33	2.5×10^{-2}

Table 3. Summary of ion-exchange data for Cd(II), Ni(II) and Ca(II) on PAA and PIA modified electrospun cellulose nanofiber membranes and other materials.

Ion exchange materials	Functional groups	Maximum static binding capacity		
		mg Cd/g	mg Ni/g	mg Ca/g
Dowex 50W	Sulfonic acid	277	75 ³⁹	-
Duolite CT-73	Thiol	106 ⁴⁰	56.9 ⁴⁰	-
Amberlite 200	Sulfonic acid	225 ⁴⁰	129 ⁴⁰	-
Ceralite IRC-50	Carboxylic acid	46.7 ⁴¹	-	-
Amberlite IRC-86	Carboxylic acid	53.8 ⁴²	1.53 ⁴³ , 2.75 ⁴⁴	-
Amberlite IRC-718	Iminoacetic acid	119 ⁴⁵ , 202 ⁴⁶	129 ⁴⁷ , 35.2 ⁴⁶	47.21 ⁴⁸
poly-L-aspartic acid-silica based-MF membrane	Amino acid	80 ⁴⁹	-	-
RC-PGMA-PAA (Whatman 60 MF membranes)	Carboxylic acid	90.7	-	-
RC-PGMA-PIA (Whatman 60 MF membranes)	Carboxylic acid	101	-	-
RC-PGMA-PAA	Carboxylic acid	162	107	85
RC-PGMA-PIA	Carboxyl acid	222	52	33

Table 4. Comparison of the experimental and calculated Q_e values evaluated from the multi-component Langmuir isotherm model for Cd-Ni and Cd-Ca ion exchange on PAA- and PIA-modified electrospun cellulose nanofiber membranes.

Sorbent material	Initial concentration (mg/L)			Equilibrium concentration (mg/L)			Experimental static binding capacity (mg/g)						Predicted static binding capacity (mg/g)		
	Cd	Ni	Ca	Cd	Ni	Ca	Cd	SD	Ni	SD	Ca	SD	Cd	Ni	Ca
RC-PGMA-PAA	10	20	-	3.5	12.5	-	19.5	3.8	25.5	3.3	-	-	18.0	22.7	-
	10	40	-	4.0	25.4	-	18.0	2.9	39.9	10.5	-	-	16.0	37.3	-
	5	20	-	1.6	12.2	-	10.2	1.0	23.3	9.0	-	-	8.6	23.7	-
	5	40	-	2.0	24.0	-	9.0	0.8	45.9	4.8	-	-	8.8	37.9	-
RC-PGMA-PIA	10	20	-	3.5	12.5	-	24.6	1.7	32.9	3.0	-	-	24.4	25.1	-
	10	40	-	4.0	25.4	-	20.9	2.4	40.9	3.7	-	-	19.6	37.2	-
	5	20	-	1.6	12.2	-	12.5	0.8	26.8	4.8	-	-	10.3	30.1	-
	5	40	-	2.0	24.0	-	12.1	2.1	52.3	5.5	-	-	7.5	38.1	-
RC-PGMA-PAA	10	-	100	4.0	-	88.6	18.0	1.2	-	-	34.1	5.9	15.0	-	33.1
	10	-	300	5.4	-	279.6	13.8	2.0	-	-	58.1	9.3	11.0	-	55.8
	10	-	500	6.3	-	466.9	11.4	2.1	-	-	94.8	3.2	8.9	-	64.3
	5	-	100	1.5	-	86.6	10.5	0.7	-	-	38.4	0.6	6.2	-	34.7
	5	-	300	1.7	-	277.8	9.5	0.3	-	-	63.1	10.8	3.7	-	58.5
	5	-	500	2.0	-	463.2	9.0	0.3	-	-	105.2	2.7	3.0	-	66.7
RC-PGMA-PIA	10	-	100	2.1	-	88.5	23.7	0.8	-	-	34.4	8.3	20.0	-	20.7
	10	-	300	4.0	-	278.8	18.0	4.6	-	-	63.5	14.3	15.5	-	26.8
	10	-	500	5.1	-	472.6	14.8	1.0	-	-	82.3	19.2	12.4	-	28.7
	5	-	100	1.0	-	86.7	12.1	1.1	-	-	40.0	10.4	9.8	-	21.6
	5	-	300	2.0	-	278.1	8.2	0.1	-	-	59.7	0.4	8.1	-	27.8
	5	-	500	2.1	-	471.1	8.7	0.9	-	-	86.8	1.6	5.4	-	29.7

Figure Captions

Figure 1. ATR-FTIR spectra of regenerated cellulose nanofiber mat (A), poly(glycidyl methacrylate) modified nanofiber mat (B), poly(acrylic acid) modified nanofiber mat (C) and poly(itaconic acid) modified nanofiber mat (D).

Figure 2. SEM images of regenerated cellulose nanofiber mats, before (A) and after (B) modification by poly(glycidyl methacrylate), after modification by poly(acrylic acid) (C) and after modification by poly(itaconic acid) (D).

Figure 3. Permeability measurements of electrospun nanofiber membranes prepared using 4 h spinning. Data are shown for PGMA coated membranes modified by PAA and PIA. Error bars represent the standard deviation between two samples.

Figure 4. Single-component ion exchange isotherms of Cd(II), Ni(II) and Ca(II) on PAA-modified electrospun regenerated cellulose nanofiber membranes.

Figure 5. Single-component ion exchange isotherms of Cd(II), Ni(II) and Ca(II) on PIA- modified electrospun regenerated cellulose nanofiber membranes.

Figure 6. Comparison of ion exchange isotherms on PAA- and PIA-modified electrospun nanofiber membranes. (a) Cd(II) in the presence of increasing Ni(II) and (b) Ni(II) in the presence of increasing Cd(II). (Solid lines represent PAA-modified membranes and dashed lines represent PIA-modified membranes.)

Figure 7. Three-dimensional binary ion-exchange isotherms on PAA-modified electrospun nanofiber membranes. The surfaces are predictions by the Langmuir model and the symbols are experimental data for Cd(II) uptake (a) and for Ni(II) uptake (b).

Figure 8. Three-dimensional binary ion-exchange isotherms on PIA-modified electrospun nanofiber membranes. The surfaces are predictions by the Langmuir model and the symbols are experimental data for Cd(II) uptake (a) and for Ni(II) uptake (b).

Figure 9. Two-dimensional binary ion-exchange isotherms on PAA-modified electrospun nanofiber membranes. Data are shown for predictions by the Langmuir model and experimental for Cd(II) uptake (a) and for Ni(II) uptake (b). Error bars in experimental data represent the standard deviation between two samples.

Figure 10. Two-dimensional binary ion-exchange isotherms on PIA-modified electrospun nanofiber membranes. Data are shown for predictions by the Langmuir model and experimental for Cd(II) uptake (a) and for Ni(II) uptake (b). Error bars in experimental data represent the standard deviation between two samples.

Figure 1. ATR-FTIR spectra of regenerated cellulose nanofiber mat (A), poly(glycidyl methacrylate) modified nanofiber mat (B), poly(acrylic acid) modified nanofiber mat (C) and poly(itaconic acid) modified nanofiber mat (D).

Figure 2. SEM images of regenerated cellulose nanofiber mats, before (A) and after (B) modification by poly(glycidyl methacrylate), after modification by poly(acrylic acid) (C) and after modification by poly(itaconic acid) (D).

Figure 3. Permeability measurements of electrospun nanofiber membranes prepared using 4 h spinning.

Data are shown for PGMA coated membranes modified by PAA and PIA. Error bars represent the standard deviation between two samples.

Figure 4. Single-component ion exchange isotherms of Cd(II), Ni(II) and Ca(II) on PAA-modified electrospun regenerated cellulose nanofiber membranes.

Figure 5. Single-component ion exchange isotherms of Cd(II), Ni(II) and Ca(II) on PIA- modified electrospun regenerated cellulose nanofiber membranes.

Figure 6. Comparison of ion exchange isotherms on PAA- and PIA-modified electrospun nanofiber membranes. (a) Cd(II) in the presence of increasing Ni(II) and (b) Ni(II) in the presence of increasing Cd(II). (Solid lines represent PAA-modified membranes and dashed lines represent PIA-modified membranes.)

Figure 7. Three-dimensional binary ion-exchange isotherms on PAA-modified electrospun nanofiber membranes. The surfaces are predictions by the Langmuir model and the symbols are experimental data for Cd(II) uptake (a) and for Ni(II) uptake (b).

Figure 8. Three-dimensional binary ion-exchange isotherms on PIA-modified electrospun nanofiber membranes. The surfaces are predictions by the Langmuir model and the symbols are experimental data for Cd(II) uptake (a) and for Ni(II) uptake (b).

Figure 9. Two-dimensional binary ion-exchange isotherms on PAA-modified electrospun nanofiber membranes. Data are shown for predictions by the Langmuir model and experimental for Cd(II) uptake (a) and for Ni(II) uptake (b). Error bars in experimental data represent the standard deviation between two samples.

Figure 10. Two-dimensional binary ion-exchange isotherms on PIA-modified electrospun nanofiber membranes. Data are shown for predictions by the Langmuir model and experimental for Cd(II) uptake (a) and for Ni(II) uptake (b). Error bars in experimental data represent the standard deviation between two samples.