

Using Chemically Modified Tanzanian Cashew Nut Shell Liquid in Sequestering Pb²⁺ and Cd²⁺ from Simulated Contaminated Water

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ABSTRACT

Cashew nut shell liquid (CNSL)-based micron-sized polymeric particles (MSPPs) of average particle sizes of approximately 0.1 μm to 0.4 μm , were prepared by formaldehyde emulsion polycondensation of technical CNSL. The technical CNSL of 820 centipoise viscosity was used. Surface chemical modifications of MSPPs were carried out to introduce appropriate functional groups for cation exchange. Through suitable reactions with monochloroacetic acid, concentrated sulfuric acid, and aminopropyltrimethoxysilane, respectively, carboxylic, sulphonic, and aminopropylsilyl functional groups were introduced onto MSPPs. Column-packed MSPPs and chemically modified MSPP were successfully used to exchange lead and cadmium ions in contaminated water. The extent of Pb²⁺ and Cd²⁺ exchanged was analysed by AAS. The amount of Pb²⁺ and Cd²⁺ exchanged by the unmodified MSPP was 0.022 mg/g and 0.034 mg / g, respectively. The amounts of Pb²⁺ exchanged by the modified resins were 0.056 mg/g, 0.023 mg / g, and 0.103 mg/g for the carboxylated, sulfonated and aminopropylsilylated MSPPs, respectively. The amount of Cd²⁺ exchanged by the carboxylated, sulfonated and aminopropylsilylated MSPPs was 0.062 mg/g, 0.093 mg / g, and 0.040 mg/g. The results suggested improvement in Pb²⁺ and Cd²⁺ exchange capacity with chemical modifications of the CNSL based polymer particles. A strong correlation between Pb²⁺ and Cd²⁺ uptake of the polymer particles and the pH of the solution is also observed. The low values of Pb²⁺ and Cd²⁺ exchanges, call for further study to optimise the resins' heavy metal ions uptake capacity

Key words: CNSL, Cation Exchange, Heavy metals, pollution, Cashew nut, Lead, Cadmium

Received: 08.03.24

Accepted: 30.09.24

1. INTRODUCTION

Proliferation of industries without the parallel establishment of appropriate facilities for effluent treatment is a serious problem in developing countries. In Tanzania, several studies have revealed the presence of heavy metals in water bodies from urban areas such as Dar es Salaam, Arusha, Moshi and Mwanza. (National Environmental Management Council, 1991; Qamara and Othman, 1996; Machiwa, 1992a, 1992b; Mashauri and Mayo, 1992). The presence of heavy metals in water bodies has mainly been associated with industrial effluents that are discharged without proper treatment. For example

Mbogo (1991) reported very high levels of lead from battery manufacturing factories in Dar es Salaam. In a different study by Bwathondi et al (1991) revealed the presence of high levels of heavy metals and toxic chemicals such as dyes and corrosive acids in effluents from food/beverages and textile factories. All of these effluents are discharged into streams and rivers that flow through industrial areas and ultimately end up in the Indian Ocean.

Comprehensive treatment of heavy-metal-contaminated wastewater must involve removal of the heavy metals. One of the efficient methods to remove

heavy metals from contaminated solutions is by using adsorbents. Some adsorbents, such as activated carbons, have been explored for this purpose in our laboratory (Mkayula and Mdoe, 1999, Gervas et al., 2016). The same laboratory also has vast experience in preparing polymeric particles from (Kayuki, 2002) and for enzyme immobilization (Mwalongo, 1998). Prospects have also been presented to utilize macro-sized and micron-sized CNSL-derived polymer beads for ion exchange applications. (Ilomo et al 2004). This is due to the versatile structural features of CNSL components that support polymerization and subsequent chemical modifications of the later polymers into specialty polymers. In this regard, there have been few attempts on the chemical modification and functionalization of CNSL based polymer beads (Ilomo et al, 2004) had chemically modified micron-sized CNSL-based polymeric beads by monochloroacetic acid treatment and observed a ten-fold increase in their capacity for Ca^{2+} adsorption. The chemically modified micron-sized CNSL-based polymeric particles are thus potential exchangers for heavy metals.

The use of synthetic polymer materials for ion exchange applications is well documented. Recent research and practical applications of polymers derived from renewable monomer resources have garnered significant interest from scientists, driven by both environmental and economic considerations (Ault, 1987; Zhang et al., 2022; Li and Chen, 2023). Studies have shown that these sustainable polymers offer promising alternatives to traditional petrochemical-based materials, contributing to reduced carbon footprints and enhanced biodegradability (Smith et al., 2021; Patel and Kumar, 2023).

In this current study, micron-sized polymer particles are prepared from technical CNSL, a source of renewable

CNSL, a cheap by-product material in cashew nut processing factories, and researching for possible applications thereof. On the basis of their good physicochemical properties, CNSL-derived polymeric particles have been used successfully for Catalytic support

natural monomers. The polymer particles are then chemically modified, to carboxylated, sulfonated, and aminopropylsilylated forms by appropriate chemical reactions. The ability of modified and unmodified polymer particles (resins) to remove Pb^{2+} and Cd^{2+} from aqueous solution of these ions is assessed at a concentration of 10 ppm.

2. MATERIALS AND METHODS

2.1 Materials

Technical CNSL was received from TANITA, a cashew nut processing industry based in Dar es Salaam. The NaOH pellets (99% purity) were purchased from Unilab Suppliers. Formalin (37-41% w / v), sodium lauryl sulfate (NaLS), hydrochloric acid, sulfuric acid, monochloroacetic acid, aminopropyltrimethoxysilane (AMPS) and toluene were analytical grade samples from BDH Chemicals Ltd.

2. 2 Methods

2.2.1 Preparation of unmodified micron-sized polymer particles (MSSPs)

Latexes of unmodified micron-sized polymer particles were prepared from technical CNSL, formaldehyde solution (formalin), and NaOH by the emulsion polycondensation technique. The procedure described by Ilomo et al (2004). was adopted with minor modifications, in which about 60 g of CNSL (viscosity 820 centipoise), approximately 1 g of sodium hydroxide as catalyst, and approximately 2 g of sodium lauryl sulfate surfactant as

emulsifier were transferred into the reactor with approximately 1000 ml of distilled water. The mixture was heated to 60 ° C under constant stirring of 600 rpm for one hour. Approximately 16 ml of formalin were then added to the mixture in the reactor to begin polymerization while the temperature was maintained at approximately 60 ° C for 6 hours under constant stirring at 600 rpm. The latexes were filtered; the residual particles were then successively washed with plenty distilled water and acetone, and then dried to powdery solids. The average particle sizes, particle size distribution, and morphology were determined by a transmission electron microscope (TEM) and cryo-SEM (scanning electron microscope).

2.2.2 Preparation of CNSL-based cation exchange resins (CER)

2.2.2.1 Preparation of carboxylated MSPPs resins

The MSPPs were modified to carboxylated resins by a reaction with monochloroacetic acid (Ault, 1987) 5 g of monochloroacetic acid were added to a mixture of 4 g of MSPP in 100 ml of 1.003 M NaOH. The mixture was heated in a steam bath until the pH was constant (about 4 hours). A constant pH reading indicated completion of the reaction.

The particles were then filtered and washed with distilled water at room temperature until the conductance of the filtrate and that of the distilled water was equal. The chloride test was also done simultaneously by adding a few drops of 0.1 M AgNO₃. The properly washed particles (residue) were made to react with 100 ml of 1 M HCl in a conical flask by heating in a water bath for at least 1 hour and constantly shaking. Finally, the mixture was cooled to room temperature and filtered. The particles were washed with distilled water until the conductance of the filtrate was equal to that of distilled

water and baked in an oven at 60 ° C overnight.

2.2.2.2 Preparation of aminopropylsilylated resin

MSPP were modified to aminopropylsilylated resin by a reaction with aminopropyltrimethoxysilane (AMPS) (Mdoe, 2000; Johnson, 2003). A sample of MSPP was oven dried at a temperature of 90 ° C for approximately 4 hours. 3 g of the dried MSPP and 1.4 g of AMPS were placed in a 100 ml round bottom flask into which approximately 20 ml of toluene was added. The mixture was stirred and refluxed (at approximately 100 ° C) in the paraffin oil bath for 24 hours. The mixture was filtered and then thoroughly washed with about 100 ml toluene and acetone successively. The resultant product was air dried at room temperature and then in an oven at ca. 90 ° C.

2.2.2.3 Preparation of sulfonated resin

Fuming conc. sulfuric acid was used to sulphonate the MSPP (Furniss et al., 1978). A mixture of 2 g MSPP and 8 g conc. H₂SO₄ was placed in a 1 litre flask fitted with a reflux condenser and heated in a water bath for 6 hours. The product was filtered, washed properly with water and acetone, and dried.

2.2.3 Exchange of lead and cadmium ions by the CNSL based cation exchange resins

Glass columns with stopcocks and porous disks were about 300 mm long and about 12 mm inner diameter. A small amount of glass wool was placed on the disk to prevent loss of the resin during sample loading. 1 g of resin, slurred in water, was then poured into the column. The bed height of the resin in the column was approximately 20 mm. One thousand ppm stock solutions of Pb²⁺ and Cd²⁺ were prepared using Perkin Elmer¹⁶ guidelines. To make a 1000 ppm Pb²⁺ solution, 1.6062 g of Pb

(NO₃)₂ was dissolved in a few milliliters of 1% (v/v) HNO₃ and then diluted to 1 litre with distilled water. To make a 1000 ppm stock solution of Cd²⁺, 1.003 g of Cd metal was dissolved in a minimum volume of (1+1) HCl and then diluted to 1 litre with 1 % (v/v) HCl. From the 1000 ppm stock solutions, normal dilutions to 10 ppm were made.

A 10-ppm metal ion (Pb²⁺ or Cd²⁺) solution was passed through the column packed with a known dry weight (about 1 g) of a particular prepared CER. The average elution rate was approximately 3 ml/ min. The concentrations of aliquots from the effluents were analyzed by AAS. After a series of five samples, a standard solution was also determined to assess the reliability of the results. For any aliquot of effluent, the difference between the amount of metal ions in that volume before and after elution gave the amount of metal ions exchanged by the resin. The total amount of metal ions exchanged is obtained as the sum of the amount exchanged in each aliquot. The exchange capacity is determined as the maximum amount of metal ions exchanged per unit of mass of resin.

d) Regeneration of saturated CER

Except for aminopropylsilylated particles in which about 300 ml of 1 M HCl followed by the same amount of 1 M NaOH was passed through the column for regeneration, carboxylated and sulphonated particles were regenerated by passing about 100 ml 3 M HCl through the column. Thereafter, the particles were washed with ca 500 ml of distilled water ready for the next ion exchange trial.

The infrared spectra of the resins in the KBr pellets were recorded with the Shimadzu IR-435 infrared spectrometer. The sizes of the resin particles were determined by the JOEL 901 transmission electron microscope and Cryo-SEM. For determination of metal ions uptake, a PerkinElmer AA-300 atomic absorption spectrometer was used.

3. RESULTS AND DISCUSSION

3.1 Preparation and functionalization of CNSL MSPPs

The CNSL-based MSPPs resin was obtained as a yellowish-brown powdered material. The sizes of the individual particles range from 0.1 µm to 0.4 µm. The three-dimensional Cryo-SEM picture (Figure 1) indicates that the MSPPs were spherical in shape. Apparently, washing and drying procedures caused coagulation of the particles and subsequent increase in particle sizes. The average particle sizes of the resins were found to depend strongly on the amount of surfactant in the reaction mixture. Chemical modification of MSPPs to the carboxylated, sulfonated, and aminopropylsilylated resins was confirmed by infrared (IR) spectral analyses, whereby the new bands not present in the spectrum of the parent MSPPs appeared in the spectra of modified resins.

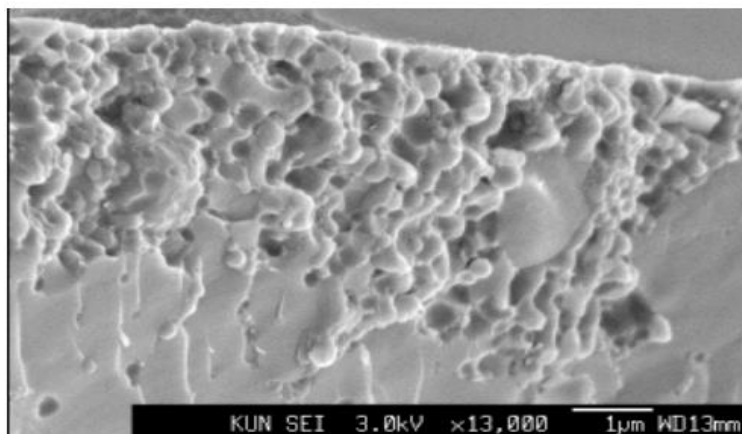


Fig 1. The three dimensional Cryo-SEM picture

The spectrum for the unmodified MSPPs (Figure 2) is characterized by a broad stretch of O-H stretch at $3500 - 3300 \text{ cm}^{-1}$ indicating the presence of phenolic O-H group, also sharp stretches of C-H stretches at 2854.5 and 2925.8 cm^{-1} which are possibly from alkyl groups present. The IR spectrum of the carboxylated resin (Figure 3) showed the presence of a sharp C=O stretch at 1650 cm^{-1} that is from the attached carboxylic COO group. The IR spectrum of aminopropylsilylated resin (Figure 4) showed N-H stretches at 3568.1 and

3375.2 cm^{-1} together with N-H bend broad peak at $1640-1560 \text{ cm}^{-1}$ indicating the presence of amino groups (AMPS group attached). There are C-H stretches at 2927.7 and 2854.5 cm^{-1} from alkyl CH stretching vibrations together with =C-H aromatic stretches at $3150-3050 \text{ cm}^{-1}$. The presence of N-H peaks in the aminopropylsilylated resin, which are absent in the parent MSPP resin, indicates that surface modification took place and was a success.

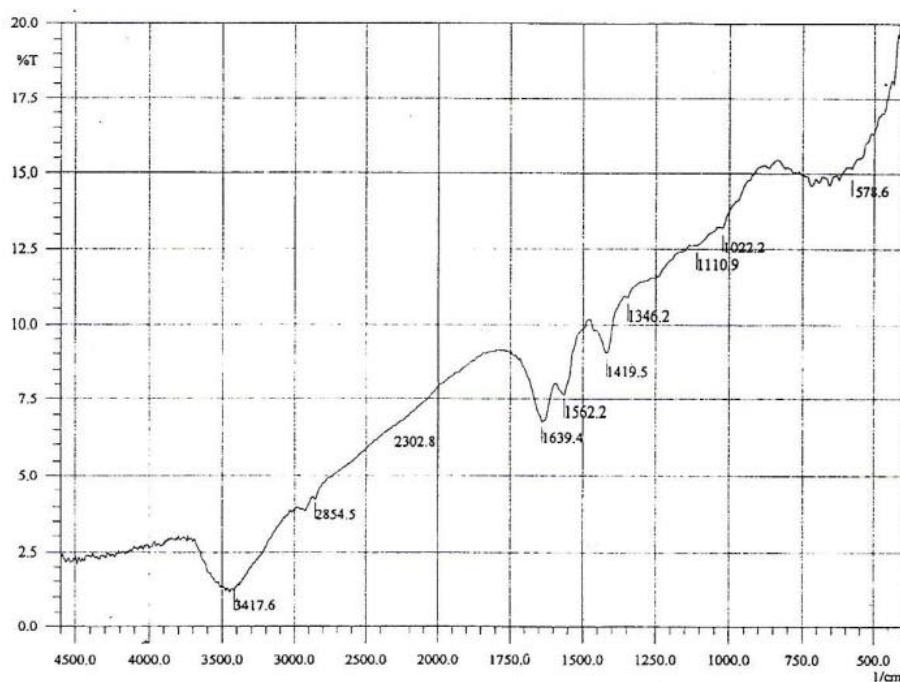


Figure 2. IR spectrum for unmodified MSPP resin

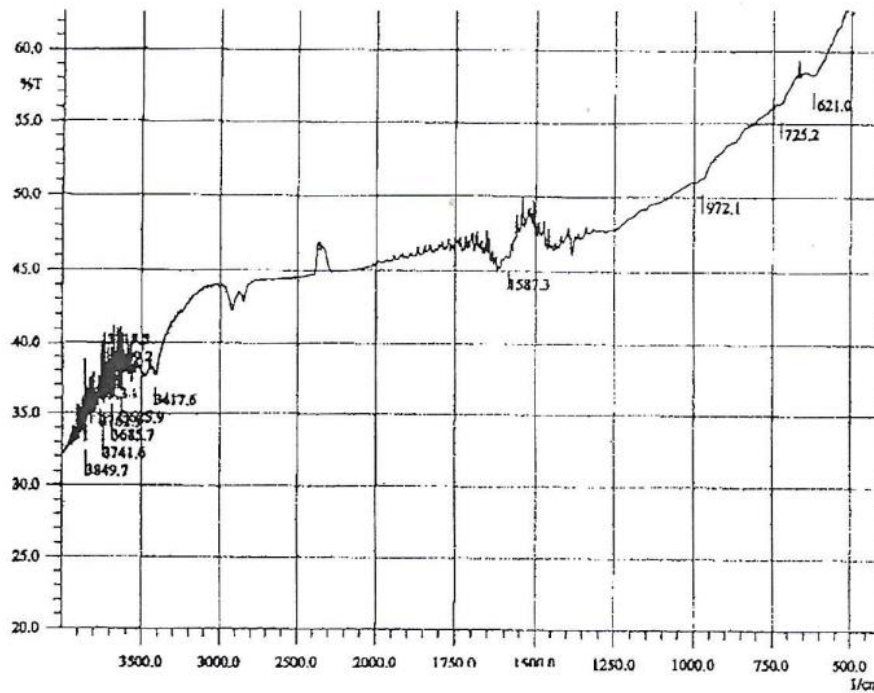


Figure 3. IR spectrum for carboxylated MSPP resin

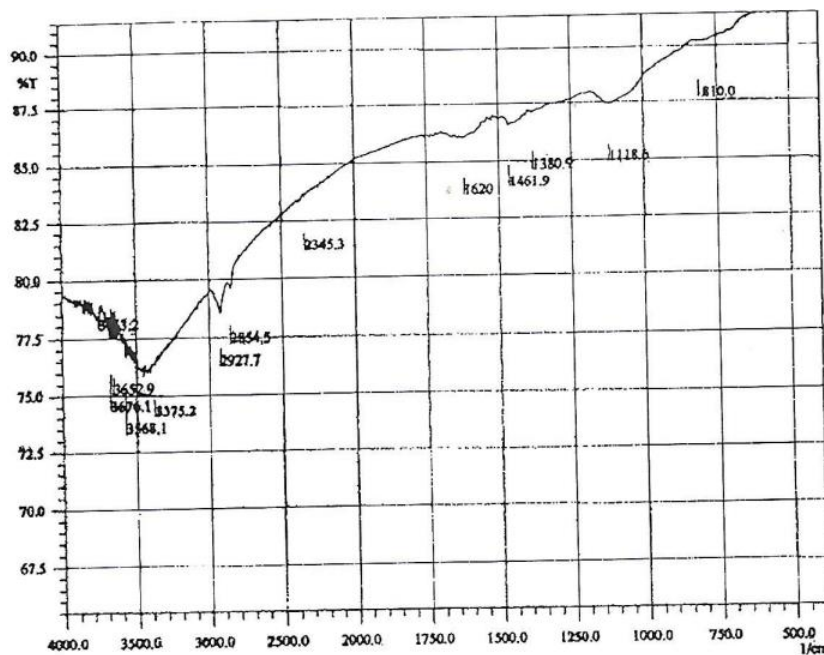


Figure 4. IR spectrum for aminopropylsilylated MSPP resin

3.2 Exchange of lead and cadmium ions by MSPP and the effect of MSPP functionalization on the cation exchange capacity

The results for the determination of the cation exchange capabilities of the different modified and unmodified resins for cadmium and lead ions are

summarized in Figures 5 & 6 and Table 1. As expected, the modified MSPP resins exchanged cadmium and lead ions relatively better than their unmodified counterparts. The unmodified MSPP resin exchanged 0.034 mg/g of cadmium ions and 0.022 mg/g of lead ions. The respective amounts of cadmium and lead ions

exchanged by the sulfonated MSPP resin were 0.051 mg/g and 0.023 mg/g. The respective amounts of cadmium and lead ions exchanged by the AMPS were

0.04 mg/g and 0.103 mg/g. Additionally, the carboxylated MSPP resin exchanged 0.093 mg/g of cadmium and 0.056 mg/g of lead

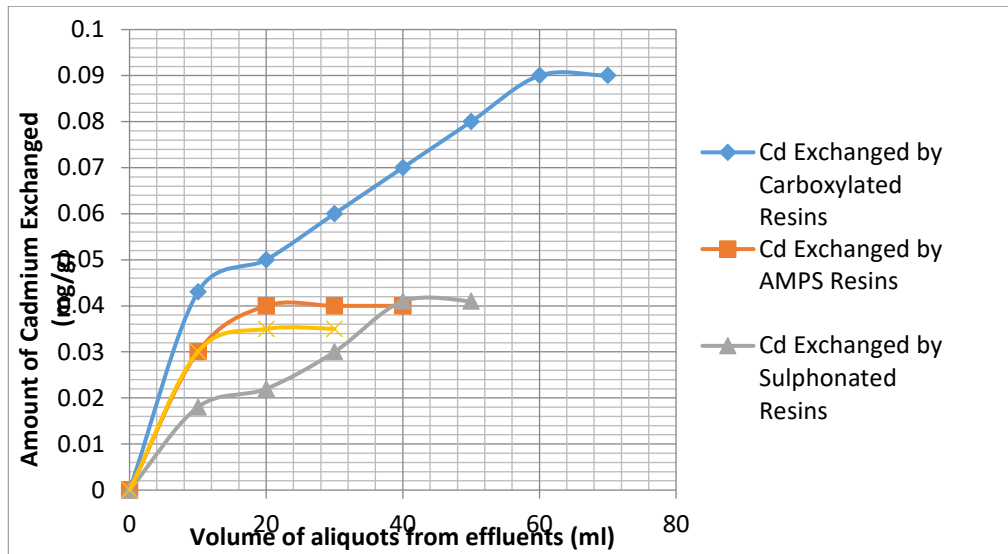


Figure 5: Cadmium exchange in specific fresh resins

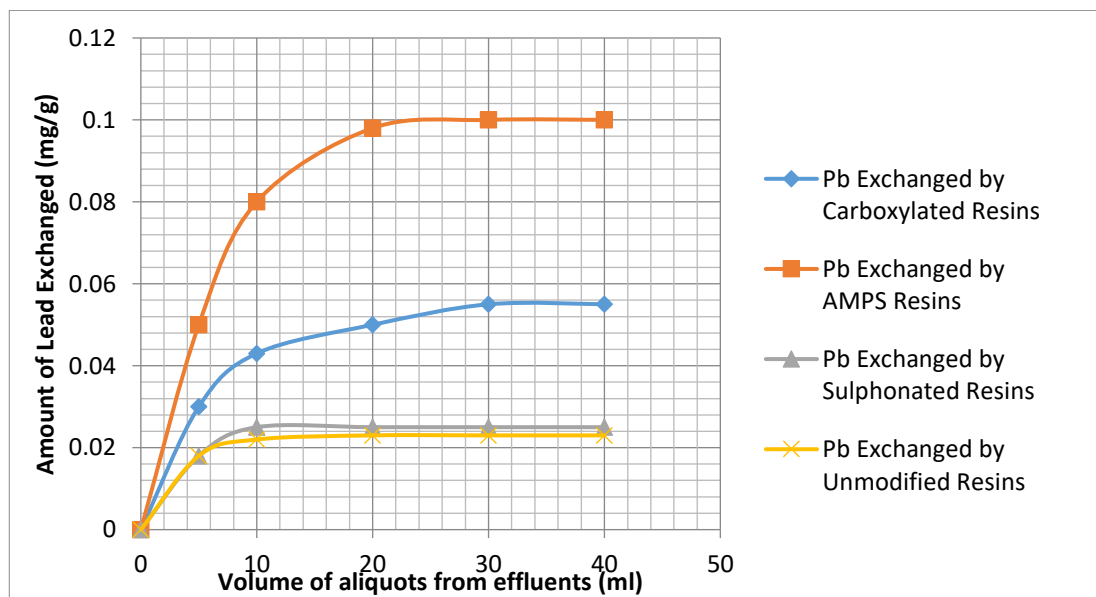


Figure 6: lead exchange in specific fresh resins

Table 1. The cation-exchange capacities of different MSPP resins

Resin type and condition	Amount of cadmium exchanged (mg/g)	Amount of lead exchanged (mg/g)
Unmodified/ Fresh	0.034	0.022
Unmodified/ Regenerated	0.029	0.029
Sulphonated / Fresh	0.051	0.023

	ed (mg/g)	
Unmodified/ Fresh	0.034	0.022
Unmodified/ Regenerated	0.029	0.029
Sulphonated / Fresh	0.051	0.023

Sulphonated/ Regenerated	0.107	0.027
Carboxylated / Fresh	0.093	0.056
Carboxylated/ Regenerated	0.079	0.066
Aminopropylsil ated / Fresh	0.040	0.103
Aminopropylsil ated /Regenerated	0.024	0.038

The carboxylated MSPP resin was found to be the best exchanger for cadmium (0.093 mg/g) as the AMPS resin was for lead (0.103 mg/g). The amount of lead exchanged by the AMPS resin was almost twice the amount exchanged by the carboxylated resin and almost five times the amount exchanged by both sulfonated and unmodified resins. The carboxylated resin exchanged cadmium almost twice as much as those exchanged by both the AMPS resin and the sulfonated resins and almost thrice the amount exchanged by the unmodified resin. The carboxylated resin exchanged cadmium relatively better than that for lead. Similarly, the sulfonated MSPP resin exchanged more cadmium (0.051 mg/g) than lead (0.023 mg/g).

When comparing the exchange capabilities of the different chemically

modified CNSL-based resins for lead and cadmium ions, it appears that the efficiency of the aminopropylsilylated resin towards lead (0.103 mg/g) is superior. The higher affinity of the AMPS resin for lead could be attributed to the mode of adsorption of that -resin. While the exchange equilibria in carboxylated and sulfonated resins are purely ionic, the exchange equilibrium in AMPS resin involves chelation through the lone pairs of N atoms in the resin. (Mdoe, 2000) A high affinity for the carboxylated resin for lead was also expected, since the acetate ion forms a highly stable complex with Pb^{2+} ion. (Shamsipur et al, 2000)

3.3 Effect of pH on the cation uptake of resins

One of the factors controlling the uptake of metal ions by cation exchange resins is the pH of influent solutions. (Samuelson, 1963) The Influence of pH on cadmium uptake by aminopropylsilylated resin is shown in Figure 7. Apparently, the optimal pH value for cadmium uptake by both the MSPP and AMPS resins is 4. Exchange experiments at higher pH values (beyond pH 6) were not performed due to the anticipated risk of hydrolysis and precipitation of the metal.

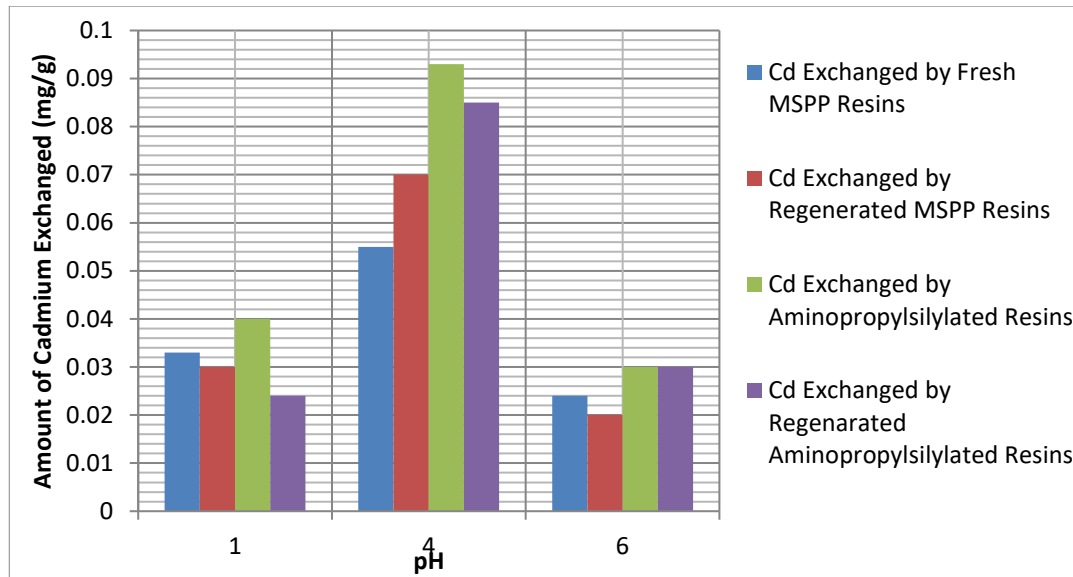


Figure 7. The influence of pH on cadmium uptake by unmodified MSPP and aminopropylsilylated resin

3.4 Effect of the elution rate on the cation uptake of the resins

The flow rate of the influent solution was also observed to affect the uptake of cations by the resins. Figure 8 shows the variation in the uptake of carboxylated resin cadmium ions when parallel exchange columns were operated at different flow rates. The average flow rates for columns A and B of similar dimensions were 2.5 ml/min and 3.9 ml/min, respectively. As shown in Figure 8 the saturation uptake for the exchange column A, operated at a flow rate of 2.5 ml/min, was approximately 0.06 mg of cadmium / g of resin, while for the

exchange column B, operated at a higher flow rate, the saturation uptake was approximately 0.08 mg of cadmium / g of resin for both fresh and regenerated resins. Apparently, the variation in cadmium uptake is due to different operating flow rates. Nevertheless, the anticipated pattern is a decline in cation absorption as the flow rate increases. However, the flow rates of the exchange columns are also influenced by the density of the resin packing. In a tightly packed exchange column, which gives low flow rates, a hindered access of ions to the exchange sites could lead to lower cation uptake.

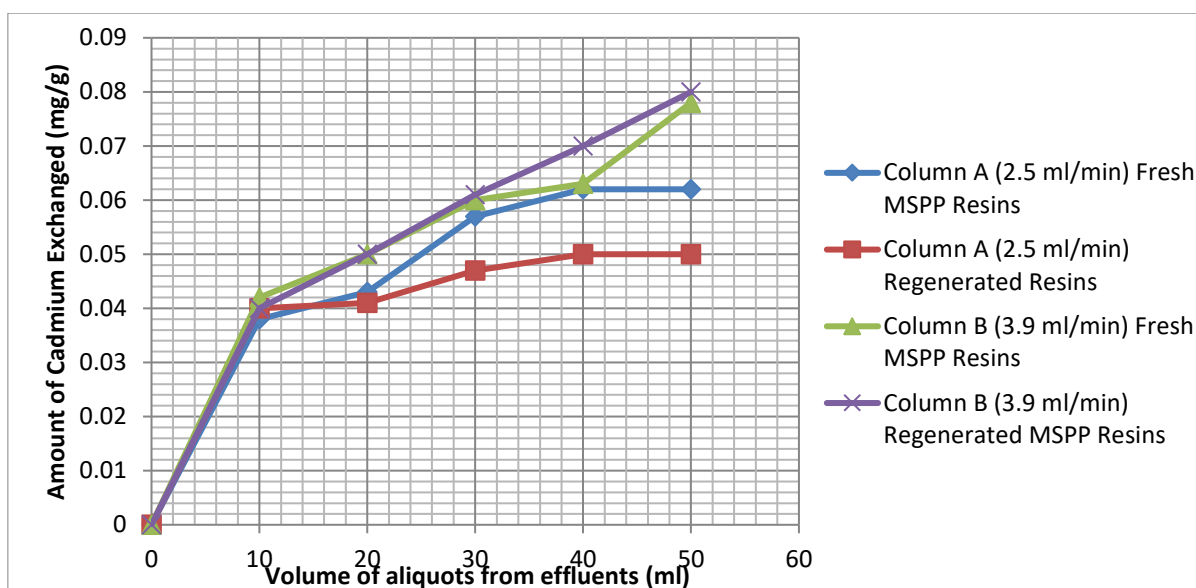


Figure 8. The effect of influent flow rate on cadmium uptake by carboxylated resin

3.5 Resin regeneration

To test for resin reusability, the resins were regenerated and subjected to additional exchange experiments. As seen in Figure 7 at low pH (pH = 1), the regenerated resins exchanged cadmium poorly compared to fresh resins, at pH 4 and pH 6, the metal uptake capacity of the regenerated resins after a circle of adsorption and regeneration is close to that of the fresh resins, thus multiple uses of the resins are feasible.

CONCLUSION

The study has indicated that while chemical modifications of the CNSL based polymer particles improved their capability to adsorb lead and cadmium (heavy metals) ions, the adsorption levels were not high enough to warrant an economical heavy metal removal process for industrial effluents. However, because a strong correlation between heavy metal uptake of the particles and the pH of the solution was observed, the optimization of heavy

metal uptake can be achieved through a systematic study of the influence of pH on the adsorption capacity of the polymer particles

Acknowledgement

The authors thank the Norwegian Agency for Development Cooperation (NORAD) for financing this work. The electron microscopy unit of the Nejmegen University is gratified for cryo-SEM micrographs. Technical assistance from members of the Chemistry Department, UDSM, is appreciated.

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