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Technical Control of Cd^{2+} from the Sludge Utilizing Cashew Nutshell Liquid Based Micron-Sized Polymeric Particles

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A B S T R A C T

This study investigated the effectiveness of micron-sized polymeric particles derived from Cashew Nutshell Liquid (CNSL) in removing cadmium cations from a laboratory-scale aquatic environment. The researchers synthesized hydroxyl-functionalized polymer particles using the emulsion polycondensation technique, with sizes ranging from 0.1 µm to 0.4 µm confirmed by Transmission Electron Microscopy (TEM). Cryo-Scanning Electron Microscopy (cryo-SEM) revealed their distinctive spherical morphology with a yellowish-brown hue. Chemical modifications (carboxylation, sulfonation, and aminopropylsilation) were achieved and confirmed through infrared (IR) spectra analysis. Atomic Absorption Spectrophotometry (AAS) evaluated the cadmium exchanging capacities of both original and modified micron-sized polymer particles in column reactions, and regeneration methods were employed for particle reusability. Unmodified and modified particles displayed substantial cadmium exchanging capacities, influenced by pH and elution rates. Modified particles, particularly sulfonated and carboxylated ones, outperformed unmodified counterparts in cadmium ion exchange. For instance, unmodified resin exchanged 0.034 mg/g, while sulfonated and carboxylated resins exchanged 0.051 mg/g and 0.093 mg/g of cadmium ions, respectively. The optimal pH for cadmium uptake was established at 4. Regenerated resins exhibited lower cadmium exchange compared to fresh resins at pH 4 and pH 6. Flow rates of influent solution and resin packing density significantly affected cation uptake. The study advocates for further research to scale up the application of CNSL-based micron-sized polymer particles for controlling heavy metal pollution in authentic aquatic environments.

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1. Introduction

The literature underscores the environmental threat posed by heavy metals (Ali et al., 2021) particularly Cadmium (Cd), due to its high toxicity (Atia-Hellal & Hellal, 2021), non-biodegradability (Shah, 2021), carcinogenic nature, and potential for bioaccumulation (Maurya, 2019). Heavy metals, including Cd, are highly soluble in aquatic environments, making their absorption into water bodies a significant concern (Kinuthia, 2020). Cadmium is identified as a key limiting factor for the use of sludge in land applications (Davis, 1984 & Achkir, 2023), and its introduction into ecosystems through industrial development raises concerns about toxicity within the broader environment (Zhang et al., 2019 & Wang et al., 2021). Common sources of Cd in urban wastewater include Ni-Cd batteries, paints, photography, food products, detergents, body care products, stormwater, ore processing plants, metal refineries' discharges, mine drainage water, waste batteries' runoff, manufacturing of phosphate fertilizers and pesticides, pigment production, printing, photographic industry, and rainwater runoff from mining areas (Ulmgren, 2000 & Samaneh, 2022). Research indicates that Cd concentrations are particularly high in tobacco, lettuce, spinach, and other leafy vegetables (Scott et al., 2019 & Ngugi et al., 2022), emphasizing the potential for human exposure through dietary intake (Davis, 1984). Consequently, there is a pressing need for effective methods to remove Cd from contaminated urban water sources (Kumar, 2015). Various techniques for heavy metal removal, including Cd, have been explored, such as solvent extraction (Suquila et al., 2019), adsorption (Awual et al., 2019), bio-adsorption (Bilal et al, 2021), ion exchange (Xiao et al., 2020), membrane filtration (Khulbe & Matsuura, 2018), chemical

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precipitation (Peng et al., 2020), and emerging electrochemical processes like bio-electrochemical systems (Kadhim & Abbar, 2022), electrocoagulation (AlJaberi & Hawaas, 2023), and electrodeposition (Samaneh, 2022).

Studies conducted regarding the Tanzanian cashew nutshell liquid (CNSL) (Mgaya et al., 2019; Mgaya & Mubofu, 2019 & Fombu et al., 2023) reveal the presence of heavy metals in water bodies and sediments of urban areas, prompting local researchers to focus on utilizing locally available adsorbent materials. Activated carbons and polymeric particles derived from CNSL have been investigated for their adsorption capabilities (Mkayula & Mdoe, 1999; Kayuki, 2002; Mwalongo, 1998; Ilomo, 2001). This study aims to modify the CNSL to create functionalized micron-sized polymer beads with enhanced adsorption capacity for Cd^{2+} cations. This involves polymerization or cross-linking to form a porous structure with increased surface area. The physical and chemical properties of these beads are crucial for understanding their adsorption efficiency. Sludge preparation includes pretreatment to remove impurities before adsorption experiments with cadmium-contaminated sludge. The study monitors adsorption kinetics and isotherms to gain insights into the adsorption mechanism and capacity. Optimization parameters include adjusting pH, temperature, adsorbent dosage, and contact time for maximal efficiency. Desorption and regeneration methods are explored to reuse loaded particles effectively.

Studies highlight the urgency of addressing Cd^{2+} contamination in water sources due to its severe environmental and health implications. Therefore, this study's focus on modifying CNSL to create efficient adsorbent materials for Cd removal presents a comprehensive approach, encompassing synthesis, characterization, adsorption experiments, and optimization, contributing to the broader efforts in environmental remediation.

2. Experimental

2.1. Reagents

The CNSL was received from Tanita, a cashew nut processing industry based in Dar es Salaam. NaOH pellets (99% purity) were purchased from Unilab suppliers in Dar es Salaam. The formalin (37-41% w/v), sodium lauryl sulphate (NaLS), hydrochloric acid, sulphuric acid, monochloroacetic acid, aminopropyltrimethoxysilane (AMPS) and toluene were analytical grade samples obtained from the BDH Chemicals Ltd in Dar es Salaam.

2.2. Methods

2.2.1 Preparation of Micron-Sized Polymer Particles (MSPP)

Micron-sized polymer particles latexes were prepared from CNSL, formaldehyde, and NaOH using the emulsion polycondensation technique. The procedure outlined by Ilomo (2001) was adopted accordingly with minor modifications. Subsequently, the latexes were filtered, and the remaining particles were washed successively with distilled water and acetone. This was followed by another round of washing with distilled water before drying the particles to powdery solids. The average particle sizes and particle size distribution were determined using Transmission Electron Microscope (TEM).

2.2.2 Preparation of CNSL-based Cation Exchange Resins (CER)

a) Preparation of Carboxylated MSPP Resins

The MSPP was modified into carboxylated resins through a reaction with monochloroacetic acid (Ault, 1987). Five grams of monochloroacetic acid were added to a mixture of 4 grams of the MSPP in 100 ml of 1.003 M NaOH. The mixture was heated on a steam bath until the pH remained constant (approximately 4 hours). The constant pH reading indicated the completion of the reaction. The particles were then filtered and washed with plenty of distilled water at room temperature until the conductance of the filtrate matched that of the distilled water. The chloride test was also conducted simultaneously by adding a few drops of 0.1 M $AgNO_3$. The properly washed particles (residue) were made to react with 100 ml of 1 M HCl in a conical flask, heated in a water bath for at least 1 hour while shaken constantly. Finally, the mixture was cooled to room temperature and filtered. The particles were washed with distilled water until the conductance of the filtrate equaled that of the distilled water. The particles were then oven-dried at 60 °C overnight.

b) Preparation of Aminopropylsilylated Resin

The MSPP was modified into aminopropylsilylated resin through a reaction with aminopropyltrimethoxysilane (AMPS) (Khanday, 2019 & Mkayula, 1999). A sample of MSPP was oven-dried at a temperature of 90 °C for about 4 hours. Three grams of the dried MSPP and 1.4 grams of AMPS were placed into a 100 ml round-bottomed flask, into which approximately 20 ml of toluene was added. The mixture was stirred and refluxed (at about 100 °C) in a paraffin oil bath for 24 hours. The mixture was filtered and then thoroughly washed with toluene and acetone successively. The resulting product was air-dried at room temperature and then in an oven at approximately 90 °C.

c) Preparation of Sulphonated Resin

Fuming concentrated sulfuric acid was used to sulphonate the MSPP (Kayuki, 2002). A mixture of 2 grams of MSPP and 8 grams of concentrated H2SO4 was placed into a 1-liter flask fitted with a reflux condenser and heated in a water bath for 6 hours with occasional shaking. The product was filtered, thoroughly washed with water and acetone, and then dried.

2.2.3 Exchange of Cadmium ions by the CNSL-based Cation Exchange Resins

a) Preparation of Exchange Resin Columns

Glass columns with stopcocks and porous disks were approximately 300 mm long and had an inner diameter of about 12 mm. A small amount of glass wool was placed on the disk to prevent the loss of 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.

b) Preparation of stock solutions of cadmium ions

The 1000 ppm Cd^{2+} stock solutions were made using Perkin Elmer procedures (Mwalongo, 1998). To create a 1000 ppm stock solution of Cd^{2+}, 1.003 g of Cd metal was dissolved in a minimal volume of (1+1) HCl and then diluted to 1 liter with 1% (v/v) HCl. From the 1000 ppm stock solutions, subsequent dilutions to 10 ppm were made.

c) Determination of Exchange Capacity of the CER

A 10-ppm metal ion Cd^{2+} solution was passed through a column packed with a known dry weight (approximately 1 g) of a specifically prepared CER. The average elution rate was about 3 ml/min. Aliquots of increasing volumes were collected as effluents, and their concentrations were analyzed by AAS. After a series of five samples, a standard solution was also determined to assess the reliability of the results. For each effluent aliquot, the difference between the amount of metal ions in that volume before and after elution provided the amount of metal ions exchanged by the resin. The total amount of metal ions exchanged is obtained by summing the amount

exchanged in each aliquot. The exchange capacity is determined as the maximum amount of metal ions exchanged per unit mass of resin.

d) Regeneration of Saturated CER

Except for aminopropylsilylated particles, which underwent regeneration with about 300 ml of 1 M HCl followed by the same amount of 1 M NaOH passed through the column, carboxylated and sulphonated particles were regenerated by passing 3 M HCl through the column. Afterward, the particles were washed with a generous amount (approximately 500 ml) of distilled water in preparation for the next ion exchange trial.

2.3. Instruments

The infrared spectra of the resins in KBr pellets were recorded using a Shimadzu IR-435 infrared spectrometer. Resin particle sizes were determined by a JOEL 901 transmission electron microscope. For the determination of metal ion uptake, a Perkin-Elmer AA-300 atomic absorption spectrometer was used.

3. Results and Discussion

3.1. Micron-sized Polymer Particles (MSPP) from CNSL Functionalization of MSPP to Carboxylated-, Sulphonated- and Aminopropysilylated Resins

The MSPP resin derived from cashew nutshell liquid was obtained as a yellowish-brown powdered material, with individual particle sizes ranging from 0.1 µm to 0.4 µm. The cryo-SEM image in Fig. 1 illustrates that the MSPP particles took on a spherical shape. Subsequent washing and drying procedures led to particle coagulation and an ensuing increase in particle sizes. The average particle sizes of the resins were notably influenced by the quantity of surfactant present in the reaction mixture. Chemical modifications of MSPP into carboxylated, sulfonated, and aminopropylsilylated resins were verified through infrared (IR) spectral analysis. In the spectrum of the modified resins, new bands emerged that were absent in the spectrum of the original MSPP, confirming the successful chemical transformations.

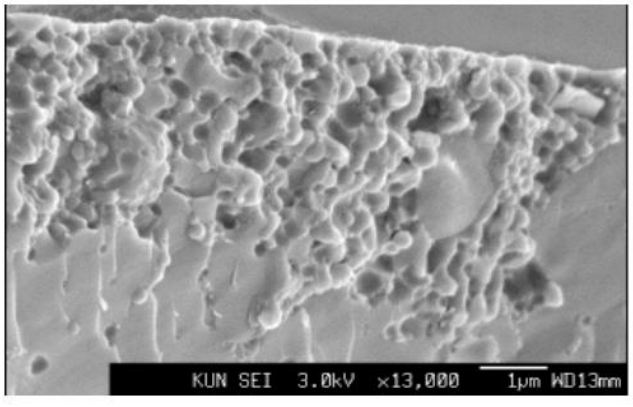


Fig. 1. Cryo-SEM Micrograph of MSPP.

The spectrum representing the unmodified MSPP (Fig. 2) exhibited a broad O-H stretch in the range of 3500-3300 cm^{-1}, suggesting the presence of a phenolic O-H group. Sharp C-H stretches at 2854.5 and 2925.8 cm^{-1} are also observed, potentially originating from alkyl groups. In the IR spectrum of the carboxylated resin (Fig 3), a sharp C=O stretch at 1650 cm^{-1} is evident, indicating the presence of the attached carboxylic COO group. The IR spectrum of the aminopropylsilylated resin revealed N-H stretches at 3568.1 and 3375.2 cm^{-1}, accompanied by a broad N-H bend peak in the range of 1640-1560 cm^{-1}, suggesting the presence of amino groups (AMPS group attached). Additionally, there are C-H stretches at 2927.7 and 2854.5 cm^{-1} resulting from alkyl CH stretching vibrations, as well as =C-H aromatic stretches at 3150-3050 cm^{-1}. The presence of N-H peaks in the aminopropylsilylated resin, absent in the original MSPP resin, indicated the successful occurrence of surface modification.

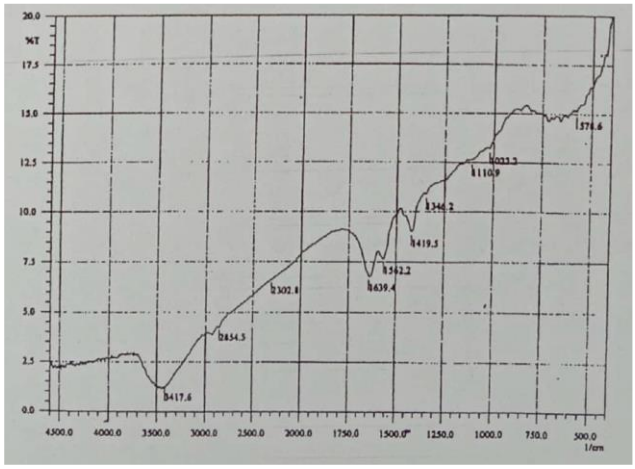


Fig. 2. IR spectrum for unmodified MSPP resin.

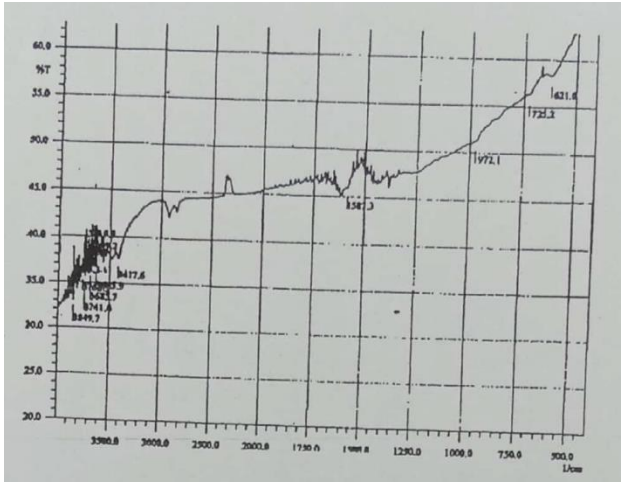


Fig. 3. IR spectrum for carboxylated MSPP resin.

3.2. Exchange of Cadmium Ions by MSPP and the Effect of Functionalization of MSPP on the Cation Exchange Capacity

The findings from the assessment of cation exchange capabilities for cadmium ions using various modified and unmodified resins are presented in Figs 4 and 5, as well as Table 1. Notably, the modified MSPP resins demonstrated more effective cadmium ion exchange compared to their unmodified counterparts. The unmodified MSPP resin exhibited a cadmium ion exchange capacity of 0.034 mg/g. In contrast, the sulfonated MSPP resin exchanged 0.051 mg/g of cadmium ions, the AMPS-modified resin exchanged 0.04 mg/g, and the carboxylated MSPP resin displayed a higher cadmium exchange capacity, reaching 0.093 mg/g.

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

Resin Type and Condition	Amount of Cadmium Exchanged (mg/g)
Unmodified/ Fresh	1. 0.034
Unmodified/ Regenerated	2. 0.029
Sulphonated / Fresh	3. 0.051
Sulphonated/ Regenerated	4. 0.107
Carboxylated / Fresh	5. 0.093
Carboxylated/ Regenerated	6. 0.079
Aminopropylsilated / Fresh	7. 0.040
Aminopropylsilated /Regenerated	8. 0.024

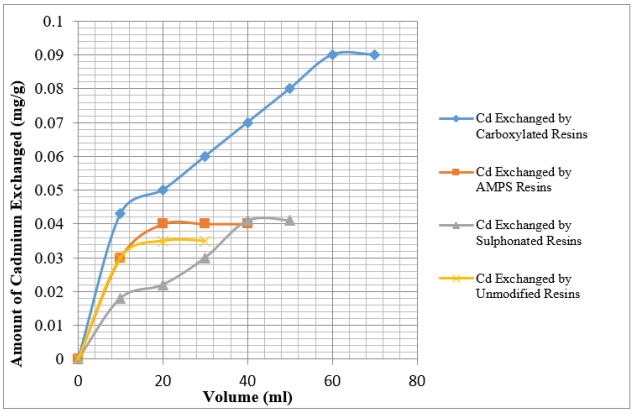


Fig. 4. Cadmium exchange in specific fresh resins.

3.3. Effect of pH on the Cation Uptake of the Resins

The pH of the influent solutions is a key determinant in regulating the absorption of metal ions by cation exchange resins, as highlighted by Mdoe (2000). Fig. 5 illustrates the impact of pH on the absorption of cadmium by the aminopropylsilylated resin. The most favorable pH for efficient cadmium uptake by both MSPP and AMPS resins is 4. Experimentation at elevated pH levels (above 6) was avoided due to the potential hazard of hydrolysis and the precipitation of the metal.

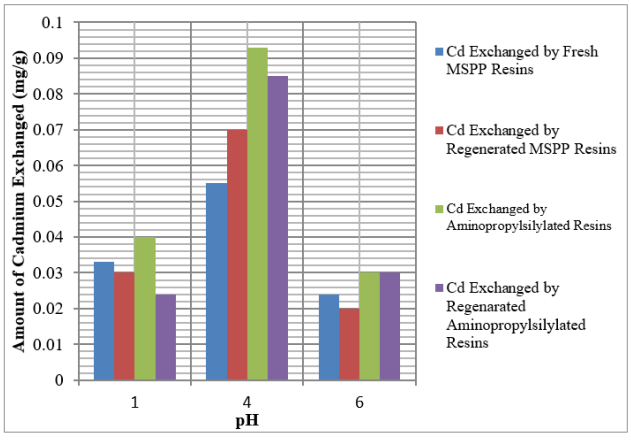


Fig. 5. The influence of pH on cadmium uptake by unmodified MSPP and aminopropylsilylated resin.

3.4 Effect of Elution Rate on the Cation Uptake of the Resins

The uptake of cations by the resins was also found to be influenced by the flow rate of the influent solution. Fig. 6 illustrates the change in cadmium ion uptake by the carboxylated resin when parallel exchange columns operated at various flow rates. Column A and Column B, both of similar dimensions, had average flow rates of 2.5 ml/min and 3.9 ml/min, respectively. As depicted in Fig. 6, the saturation uptake for exchange column A (operating at 2.5 ml/min) was approximately 0.06 mg cadmium/g resin, while for exchange column B (operating at a higher flow rate), the saturation uptake was about 0.08 mg cadmium/g resin for both fresh and regenerated resins. The observed variation in cadmium uptake is attributed to the different operational flow rates. The anticipated trend, however, is a decrease in cation uptake with an increase in flow rate. It is essential to note that the flow rates of the exchange columns are also influenced by the compactness of resin packing. In tightly packed exchange columns, resulting in lower flow rates, hindered access of ions to the exchange sites could result into a reduction in cation uptake.

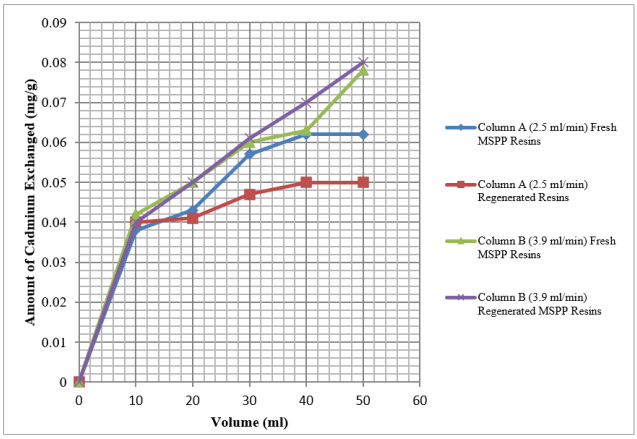


Fig. 6. The effect of influent flow rate on cadmium uptake by carboxylated resin.

3.5 Resin Regeneration

To assess resin reusability, the resins underwent regeneration and were then subjected to additional exchange experiments. Fig. 5 demonstrates that at a low pH (pH = 1), the regenerated resins exhibited poorer cadmium exchange compared to the fresh resins. However, at pH 4 and pH 6, the metal capacity of the regenerated resins, after a cycle of adsorption and regeneration, closely resembled that of the fresh resins. This suggests that multiple uses of the resins are feasible, particularly at pH levels of 4 and 6.

4. Conclusion

Fundamentally, the use of CNSL-based micron-sized polymeric particles for the sequestration of Cd^{2+} from sludge offers a sustainable and potentially cost-effective method for heavy metal removal. However, the success of the process depends on the material's adsorption capacity, the efficiency of regeneration, and the overall economic feasibility of scaling up the technology. In this study, CNSL-based micron-sized polymer particle resins have been successfully prepared and chemically modified. Cadmium cations exchanging capacities of the modified CNSL-based micron-sized polymer particle resins were relatively improved compared to their unmodified counterparts. The previously regenerated and reused micron-sized polymer particle resins demonstrated significant cadmium-exchanging capacities. Thus, the remarkable cation exchange capacities of the micron-sized polymer particle resins on the lab scale call for more

systematic upscaling study in real marine polluted environments. The next studies will explore the effect of the prepared resins based on a comparative analysis of different heavy metals to simulate real polluted water systems in urban settings.

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