Removal of Pb2+ and Cd2+ from Aqueous Solutions using POCl3 Cross-linked Carboxymethyl Derivatives of Legume Starch

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Removal of Pb\textsuperscript{2+} and Cd\textsuperscript{2+} from Aqueous Solutions using POCl\textsubscript{3} Cross-linked Carboxymethyl Derivatives of Legume Starch

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Abstract

Starch was extracted from Kwakil beans and cross-linked with POCl\textsubscript{3} (1% v/w of starch dry basis [db]). The cross-linked starch (PCS) derivative was carboxymethylated with sodium monochloroacetate (5% to 30% w/w of starch db) to obtain cross-linked carboxymethyl starch (PCCS) derivatives. The derivatives were used in the adsorption of Pb\textsuperscript{2+} and Cd\textsuperscript{2+}, and the process was monitored using atomic adsorption spectrometer. Carboxymethylation enhanced adsorption of ions (Cd\textsuperscript{2+}, 95% to 96%; Pb, 65% to 94%), and it was more appreciable with Pb\textsuperscript{2+} than Cd\textsuperscript{2+} as degree of substitution increased from 0.008 to 0.052. This was attributed to selective ion exchange, steric and stereoochemical effects of the carboxymethyl groups. Derivatives were characterized with Fourier transform infrared spectroscopy, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. Adsorption increased with pH and adsorbent dosage but decreased when temperature and interfering ion (i.e., Na\textsuperscript{+} and Ca\textsuperscript{2+}) concentrations increased. Adsorption equilibrium was reached in 5 min. Kinetic parameters of Pb\textsuperscript{2+} fitted the pseudo-second-order model ($R^2 = 0.9999$), while Cd\textsuperscript{2+} fitted the pseudo-first-order model ($R^2 = 0.9978$). Isotherm parameters of Pb\textsuperscript{2+} fitted Langmuir model ($R^2 = 0.9989$), while Cd\textsuperscript{2+} fitted Freundlich model ($R^2 = 0.9689$). These parameters inferred the involvement of different combinations of physiosorption and chemisorption mechanisms in the adsorption of Pb\textsuperscript{2+} and Cd\textsuperscript{2+}. However, the thermodynamic parameters indicated the dominance of the physiosorption mechanism in the overall exothermic process ($\Delta H = -15.51$ and $-9.79$ kJ mol\textsuperscript{-1} for Pb\textsuperscript{2+} and Cd\textsuperscript{2+}, respectively). Pb\textsuperscript{2+} and Cd\textsuperscript{2+} were recovered ($\approx$100%) in 1 M HNO\textsubscript{3}, and efficient re-adsorption (>80%) was obtained till third reuse cycle. Product was used to treat wastewater and the heavy metals were efficiently removed.

Keywords: adsorption, carboxymethyl, cross-link, Legume starch, Pb\textsuperscript{2+} and Cd\textsuperscript{2+} removal

Introduction

Heavy metals are stable, non-biodegradable, environmentally persistent, and life-threatening water contaminants [1–3]. The increasing release of heavy metals to environmental waters that accompanies industrial growth is a teeming global challenge [3, 4]. This challenge has been addressed by employing several water treatment technologies, such as biosorption, chemical precipitation, electrochemical treatment, ion exchange, membrane filtration, electrodialysis, reverse osmosis, complexation, electrode positioning, liquid–liquid extraction, oxidation–reduction process, and evaporation [1, 2, 4–6]. The increasing preference for biosorption among other techniques is based on its low cost, high efficiency, easy handling, availability, renewability, and easy recovery of heavy metal ions [5]. Starch is an abundant biopolymer with physicochemical properties that can be modified through various procedures tailored to obtain derivatives with specific physicochemical properties required in different applications [7]. Starch derivative biosorbents are functionalized to adsor dyes and heavy metal ions from aqueous media. This is typically achieved by enhancing structural stability (via cross-linking) and introducing functional groups, such as xanthate, carbonyl, carboxylate, carbamate, acrylate, and phosphate, with chelating, electrostatic, and physical trapping abilities (ultrafiltration) into the starch granule [1–4, 8–9].

The advantages of starch derivatives over other biosorbents include the possibilities of rapid fixation of pollutants, fast and easy regeneration, efficient pollutant recovery, antimicrobial activities, and renewability [8–14]. In previous studies, the removal of heavy metals from aqueous solutions using starch derivatives has been attributed to a combination of processes, including chelation, ion exchange, electrostatic interactions, hydrogen bonding, and physical entrapment of metal ions (i.e., ultrafiltration) [2, 4, 8, 9, 14, 15]. Gou et al. [9]
prepared epichlorohydrin (ECH) cross-linked corn starch phosphate carbamates (CSPC) and used to remove Pb\(^{2+}\) from aqueous solutions. The adsorption process was reported to be fast (attained equilibrium at approximately 20 min) and endothermic and to fit the Langmuir isotherm model at equilibrium. Meanwhile, the adsorption capacity was dependent on the pH of the solution, CSPC dosage, and initial concentration of Pb\(^{2+}\). Xiang et al. [4] treated ECH cross-linked starch to obtain dithiocarbamate (DTC)-modified starch (DTCS), DTC enzymolysis starch (DTCES), and DTC mesoporous starch (DTCMS). The order of adsorption capacity was DTCMS > DT CES > DTCS. Meanwhile, for each derivative, the order of heavy metal ion adsorption was Cu\(^{2+}\) > Ni\(^{2+}\) > Cr\(^{3+}\) > Zn\(^{2+}\) > Pb\(^{2+}\). The adsorption process was fast (approximately 30 min), and the adsorption kinetics fitted the pseudo-second-order model. The adsorption capacity of cross-linked potato starch xanthate for Pb\(^{2+}\) and Cd\(^{2+}\) was investigated [15]. Pb\(^{2+}\) was more adsorbed than Cd\(^{2+}\), and the adsorption data fitted the Freundlich isotherm model [15]. Sabaa et al. [14] synthesized starch-g-poly(N-vinylimidazole) and reported the adsorption (Co\(^{2+}\) > Cu\(^{2+}\) > Cd\(^{2+}\)) and antimicrobial activities of the derivative. Wang et al. [2] synthesized ECH cross-linked carboxymethyl corn starches, with the degree of substitution (DS) range of 0.43–0.59. The adsorption of Pb and Ni onto the derivative increased with the DS and solution pH, whereas the adsorption of other heavy metal ions followed the order: Pb\(^{2+}\) > Cu\(^{2+}\) > Cd\(^{2+}\) > Zn\(^{2+}\) > Ni\(^{2+}\). Phosphorus oxychloride (POCl\(_3\)) cross-linked carboxymethyl corn starch with the DS range of 0.02–0.08 was investigated for the adsorption of Cu\(^{2+}\), Pb\(^{2+}\), Cd\(^{2+}\), and Hg\(^{2+}\) by Kim and Lim [8]. Their results were similar to those of Wang et al. [8]; however, their adsorption rate (10 min) was faster than that of Wang et al. [8].

As adsorbents, studies on legume starches (crystallographically classified as Type C starches) are scarce, whereas studies on corn, potato, cassava, yam, and rice starches (crystallographically classified as Type A or B starches) are extensive [12]. Studies of legume starches can also be justified by the fact that the functional and physicochemical properties of starch derivatives depend on the botanical source of the starch, among other factors [16, 17].

Kwakil bean is a locally cultivated and underutilized variety of kidney beans (Phaseolus vulgaris L.). Its consumption has been considerably limited because of its high poisoning tendency [18, 19]. Thus, its cultivation and industrial application are limited. In this study, native starch (NS) extracted from Kwakil beans was cross-linked using POCl\(_3\) and treated with sodium monochloroacetate (SMCA) to obtain POCl\(_3\) cross-linked carboxymethyl starch (PCCS) derivatives. The starch derivatives were characterized as biosorbents for the removal of Pb\(^{2+}\) and Cd\(^{2+}\) from aqueous solutions. This study focuses on the potentials of legume starch (being with the unique morphology), as aqueous heavy metal adsorbents in the bid to encourage the diversification of starch sourcing and production for nonfood industrial application.

### Materials and Methods

#### Materials

Materials. Kwakil beans were obtained from Mangu, Plateau State, Nigeria. POCl\(_3\), SMCA, and dimethyl-sulfoxide (DMSO) were purchased from Sigma-Aldrich Chemicals (St. Louis, MO, USA). Lead nitrate (Pb(NO\(_3\))\(_2\)), cadmium nitrate (Cd(NO\(_3\))\(_2\)), hydrochloric acid (HCl), nitric acid (HNO\(_3\)), sodium hydroxide (NaOH), calcium hydroxide, potassium iodide, and ethanol absolute were supplied by Merck (Darmstadt, Germany). Meanwhile, Whatman No. 41 filter paper and fine mesh muslin cloths were obtained from local chemical stores. All chemicals are of analytical/synthesis grade. Wastewater samples were obtained from a crude oil exploration site (untreated produced water) in Forcards Terminal, Oguilagha, Burutu Local Government, Delta State, Nigeria, and a gold processing site in Nasara-Kanji, Kashegu Local Government, Niger State, Nigeria.

#### Extraction and evaluation of starch

Wet extraction of bean starch was conducted in alkaline medium by modifying Method C reported by Schoch and Maywald [20]. Cleaned beans (1 kg) were soaked overnight in 4 L of 0.5% NaOH solution, dehulled manually, and wet milled in a blender at low speed with ice-cold 1% NaOH solution. The slurry obtained was transferred in batches to a fine mesh muslin cloth, steeped, and gently squeezed to filter into 5 L of distilled water. The suspension obtained was poured through doubled muslin cloths, and the pH was adjusted to 8.0 by adding 0.1 M NaOH solution. After standing for approximately 5 h, a clear separation was obtained. The supernatant was carefully decanted, and the slurry was re-dispersed, washed in distilled water three times, filtered through Whatman No. 41 filter paper, dried in the oven overnight at 40 °C, and ground in a mortar to a fine powder. Percentage of starch yield was calculated from the mass of starch obtained with respect to the mass of beans soaked. Proximate analysis was conducted according to official methods [21]. The amylose content of native starch was determined by the iodine binding method. The starch sample (1 mg) was shaken in 6 mM iodine solution composed of 90% DMSO and 10% water until complete dissolution was obtained (in approximately 7 h). The resultant solution was diluted further with eight parts deionized water and left to stand for 30 min for the iodine–amylose complex to form a stable color. The absorbance of the solution and that of the amylose standards were read at 620 nm against the reagent blank using a UV spectrometer [22]. Three replicate experiments were conducted for each analysis.

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Cross-linking and carboxymethylation of starch. The method reported by Kim and Lim [8] was slightly modified as follows: NS (100 g, dry basis [db]) was dispersed in 300 mL distilled water in a beaker and continuously stirred using a magnetic stirrer, pH meter (Hanna HI98127) was set in contact with the slurry, while the pH was adjusted to 11.5 with 3% NaOH solution. POCl₃ (1 mL) from a micropipette was added dropwise to the slurry over the first 10 min while the pH was maintained at 11.5 with NaOH solution throughout the reaction that lasted for 1 h at room temperature (25 °C). The slurry was filtered through Whatman No. 41 filter paper, washed three times in 400 mL double distilled water, and dried in the oven at 40 °C to obtain PCS. In another round of the reaction, PCS after filtration was dispersed in 300 mL ethanol absolute, sealed, and stirred in a thermostatic water bath at 50 °C. NaOH (40 mL of 40% solution) was added dropwise for approximately 15 min before adding SMCA (5%, 10%, 15%, 20%, and 30% w/w, based on starch db) and NaOH addition was continued for 1 h. The mixture was stirred continuously in a sealed container, and the reaction was allowed to proceed for 2 h, after which the slurry was filtered, washed three times in 400 mL distilled water, adjusted to pH 8.0, and dried in the oven at 40 °C to obtain PCCS.

Determination of the degree of substitution. The degree of carboxymethyl group substitution in PCCS was determined using back titration method, as described by Stojanovic et al. [23], with slight modification according to Kim and Lim [8]. PCCS (3 g, db) was dispersed in 20 mL of deionized water and HCl (3%) was added to the slurry to reduce the pH to 2.0. The slurry was stirred for 10 min to convert the carboxymethyl group into its hydroxyl-free acid derivative. The starch was filtered, re-dispersed, washed three times in 40 mL de-ionized water, and gelatinized by boiling in the thermostatic water bath for 30 min. The gelatinized free acid derivative was titrated with the standardized 0.1 M NaOH solution. PCS was used as a blank. The experiment was repeated three times for each derivative, and the mean titer value was used to calculate n_{COOH}, which was further used to calculate the DS, as shown in Eq. 1, where M_{db} is the mass of starch db and n_{COOH} is the number of moles of the free acid derivative:

$$DS = \frac{n_{COOH} \times 162 \text{ g} \cdot \text{mol}^{-1}}{M_{db} - n_{COOH} \times 58 \text{ g} \cdot \text{mol}^{-1}}$$

Characterization. The PerkinElmer Fourier transform infrared spectrophotometer (FTIR) England, UK was used with KBr pellets in the wavelength range of 4000–500 cm⁻¹, and 10 replicate scans were run. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) characterizations were conducted with the Esprit 2.0 software (Bruker Nano GmbH, Berlin, Germany) equipped with a field emission source operating at an accelerating voltage of 15 kV. Concentrations were determined using an atomic adsorption spectrometer (AAS; Buck Scientific 210 VGP). Pb²⁺ and Cd²⁺ were scanned at 217.0 and 228.8 nm wavelengths, with detection limits of 0.06 and 0.02 ppm, respectively. A flame emission spectrometer (FES; Jenway PFP7) was used to determine the Na⁺ concentration, with the detection limit of 0.10 ppm.

Adsorption experiments. Stock solutions (1,000 ppm) of Pb²⁺ and Cd²⁺ were prepared in deionized water from pure grades of Pb(NO₃)₂ and Cd(NO₃)₂. These stock solutions were diluted to 50 ppm and other concentrations used in the adsorption experiments. Batch adsorption equilibrium was attained by shaking 1% w/v of adsorbent in aqueous solutions at 100 rpm on an orbital shaker (CelTech KJ-201BD), with the designated pH, time, and temperature, and filtering through a Whatman No. 41 filter paper. Adsorption was determined from the initial and final concentrations of ions in the filtrate solution as analyzed using AAS and FES (for Na⁺). Each adsorption experiment was performed twice, and the mean value was used to calculate the percentage adsorption (Eq. 2) and amount adsorbed (Q) in mg/g (Eq. 3):

$$\% \text{ adsorption} = \frac{(C_0 - C_e) \times 100}{C_0}$$

$$Q (\text{mg} \cdot \text{g}^{-1}) = \frac{(C_0 - C_e)V}{1,000W}$$

Where C₀ is the initial concentration, Cₑ is the equilibrium/final concentration, V is the volume of aqueous solution in mL, and W is the weight of adsorbent in g.

The effect of pH on adsorption was determined by shaking the adsorbent (1% w/v) in aqueous solutions within the pH range of 2–8 for 120 min at 30 °C. The solution pH was adjusted with 0.1 M solutions of NaOH and HCl. The adsorption rate and the effect of time were analyzed within 2–240 min at 30 °C and optimum pH, and the kinetic studies were conducted by analyzing adsorption using the pseudo-first-order, pseudo-second-order, external diffusion, and intra-particle diffusion models [6, 24–26]. The effect of initial ion concentration was analyzed within 10–200 ppm at 30 °C and the optimum pH and time. Adsorption isotherms were investigated by evaluating the adsorption data using the Langmuir, Freundlich, and Temkin isotherm models [6, 12, 27]. The effect of temperature was analyzed within 30 °C to 70 °C at the optimum pH and time. Thermodynamic studies were conducted by analyzing data using the van’t Hoff’s and thermodynamic equations. The effect of adsorbent dosage was analyzed by varying the dosage from 0.5% to 3%. Meanwhile, ionic interference was investigated using different concentrations (i.e., 5–50 ppm) of NaCl and CaCl₂ at optimum pH and time.
Desorption/regeneration and reusability studies. This study was conducted by modifying the method reported by Kim and Lim [8]. PCCSs (1 g) loaded with Pb\(^{2+}\) and Cd\(^{2+}\) after the adsorption processes were dispersed in 40 mL deionized water in two different beakers and adjusted to pH 2.0 using 1 M HNO\(_3\) solution. The slurries were stirred for 5 min, filtered, washed twice, adjusted to pH 8.0, and dried in the oven at 40 °C to obtain the regenerated PCCSs. Desorbed Pb\(^{2+}\) and Cd\(^{2+}\) concentrations in the corresponding filtrates were determined using AAS. Each experiment was conducted twice, and the mean value was used to calculate the metal ion recovery using Eq. 4. The experiment was repeated, with stirring for 10 and 15 min, and the regenerated PCCSs obtained at optimum metal ion recovery over five cycles were used in reusability studies.

\[
\% \text{ recovery} = \frac{C_{\text{desorption}}}{C_0 - C_{\text{ sorption}}} \times 100
\]

(4)

Where \(C_0\) is the initial concentration, \(C_{\text{ sorption}}\) is the concentration after adsorption, and \(C_{\text{ desorption}}\) is the concentration after desorption.

Preparation of wastewater samples for Pb\(^{2+}\) and Cd\(^{2+}\) removal using PCCSs. Wastewater samples were collected in clean PET bottles (rinsed with conc. HNO\(_3\), and deionized water), and concentrated HNO\(_3\) (10 mL/L) was added. In the laboratory, the samples were filtered using Whatman No 41 filter paper and digested as follows: 100 mL of the sample was measured into beakers, concentrated HNO\(_3\) (2 mL) and HCl (1 mL) were added to the sample in each beaker, covered with watch glass and heated on a hotplate at 90 °C for 160 min (to obtain a clear solution). The solution obtained from each sample was allowed to cool down to room temperature, filtered through Whatman No. 41 filter paper, and transferred to a 100 mL volumetric flask. Then deionized water was added up to the mark of the volumetric flask. The pH of the solutions in volumetric flasks was adjusted to 6 using 3% NaOH, before some heavy metal content were analyzed using AAS. The adsorption process was conducted using 1 % (w/v) PCCS and three replicate adsorption experiments were performed on each wastewater sample.

Statistical analysis. The Statistical Package for the Social Sciences (Version 22) was used to analyze the results. The results were expressed as the mean ± standard deviation (SD) and compared using one-way analysis of variance followed by Duncan’s multiple range test.

Results and Discussion

Starch yield and purity. The yield of starch extracted from the legume was 38%. The purity of starch was determined from its proximate composition. Moisture, protein, crude fiber, ash, fat, and carbohydrate contents were obtained as 4.69 ± 0.31%, 0.08 ± 0.02%, 0.14 ± 0.01%, 0.11 ± 0.03%, 0.82 ± 0.05%, and 92.89 ± 0.82%, respectively. The results fall within the ranges reviewed for legume starches [28]. The amylose content (36.8%) also falls within the range of 30.2% to 41.7% reported for some \textit{P. vulgaris} cultivars [28, 29].

Degree of substitution. The DS obtained after treating the cross-linked starch with different amounts of the carboxymethylating agent (i.e., SMCA) is presented in Table 1. Cross-linking is responsible for the generally low DS obtained for the carboxymethyl derivatives, and the gradual increase in the DS is due to increasing access to the OH groups actively available for interaction, as the amount of SMCA increased [2, 8]. The values obtained for DS in this study are relatively lower than those of cross-linked carboxymethyl corn starch reported by Kim and Lim [8]. This finding can be attributed to the differences in granule composition (amylose content, amylpectin ratio, and presence of non-starch constituents) and morphology [30]. POCI, is characterized by a rapid granular surface predominant reaction [31, 32]. This may limit mass transfer to the core of the starch granule and thereby lower DS.

Adsorption of aqueous ions. PCS and PCCS were used in the adsorption of Pb\(^{2+}\) and Cd\(^{2+}\), as presented in Figure 1a. PCS exhibited higher adsorption capacity for Cd\(^{2+}\) than Pb\(^{2+}\). The introduction of the carboxymethyl functionality (in PCCS-5%) resulted in a sharp increase in the adsorption of Pb\(^{2+}\) from 64.72% to 94.37%. The increase in the carboxymethyl group substitution in the derivatives (0.008–0.052) gradually increased the adsorption capacity from 94.37% to 98.19% on PCCS-20%. A similar report was made by Kim and Lim [8] for cross-linked carboxymethyl corn starch derivatives used in the adsorption of Cu\(^{2+}\). This effect was attributed to the increasing chelation and sodium ion exchange on the carboxymethyl group (–CH\(_2\)COONa) as the group was increasingly substituted onto starch derivatives. There was a slight increase in the adsorption of Cd\(^{2+}\) on PCCS-5%. Further increase in DS however decreased the adsorption of Cd\(^{2+}\) on PCCS derivatives. The decrease in the adsorption of Cd\(^{2+}\) can be attributed to the reduction in surface/nonbonded–OH groups on the derivatives as the DS of the carboxymethyl group increased [33]. The phenomenon can also be attributed to the selective ion exchange and the steric

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<th>% SMCA</th>
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<td>10</td>
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\[\text{C}_0 - \text{C}_{\text{sorption}}\]
skeletal stereochemical effects of the carboxymethyl group. Mutual polarization of cation and ligand contributes to the formation of a stable complex by augmenting the energy of attraction based on basicity [34]. Pb\textsuperscript{2+} was reported to form better mutual polarization with carboxylic groups (–COO\textsuperscript{−}) than Cd\textsuperscript{2+} [33]. This may also explain the higher adsorption of Pb\textsuperscript{2+} than Cd\textsuperscript{2+}. Combinations of chemisorption (e.g., chelation and ion exchange) and physisorption (e.g., ion trapping in the polymer matrix) mechanisms can be involved in the adsorption of ions onto starch derivatives [4]. The results obtained in this study showed that the mechanisms involved in the adsorption of Pb\textsuperscript{2+} and Cd\textsuperscript{2+} onto starch derivatives are different.

The concentrations of Na\textsuperscript{+} in remnant solutions (Figure 1b) were used to evaluate the extent of sodium ion exchange involved in the adsorption of Pb\textsuperscript{2+} and Cd\textsuperscript{2+} onto the PCCS derivatives. The adsorption of Pb\textsuperscript{2+} was accompanied by increasing Na\textsuperscript{+} concentrations in the remnant solutions. This phenomenon indicates a possible ion exchange mechanism in which sodium ions on–CH\textsubscript{2}COO\textsuperscript{−}Na\textsuperscript{+} are displaced to bind Pb\textsuperscript{2+}. The molar ratio of Na\textsuperscript{+} to Pb\textsuperscript{2+} on the derivative with the highest adsorption capacity was calculated to be 2:2.25, showing that more Pb\textsuperscript{2+} ions are adsorbed than expected in the theoretical ion exchange ratio of 2:1 for monovalent and divalent ions. This boost in the corresponding amount of Pb\textsuperscript{2+} indicates the involvement of other physicochemical processes in the overall Pb\textsuperscript{2+} adsorption process [4,8]. There was no tangible change in the Na\textsuperscript{+} concentration in the Cd\textsuperscript{2+} remnant solution as the carboxymethyl group increases in the PCCS derivatives. This finding showed that Na\textsuperscript{+} ion exchange may not be involved in the adsorption process of Cd\textsuperscript{2+} as it is in that of Pb\textsuperscript{2+}.

**Fourier-transform infrared spectroscopy.** FTIR characterization of NS, PCS, and PCCS is presented in Figure 2a. The NS spectra show a broad band between 4,000 cm\(^{-1}\) and 3,200 cm\(^{-1}\) and a narrow band at 2,923.23 cm\(^{-1}\) because of O–H and C–H vibrations, respectively. The bands at 2,195 and 1,671.15 cm\(^{-1}\) can be attributed to minor components (i.e., lipids and proteins) and water molecules associated with native starch respectively. The broad band between 1,250 cm\(^{-1}\) and 1,000 cm\(^{-1}\) can be attributed to overlaps of C–OH, C–C, and C–O–C stretching vibrations, whereas the weak peak at 885.88 cm\(^{-1}\) can be attributed to the rotational vibration of C–O bonds characteristic of polysaccharides [22,35,36]. The PCS spectra show the effect of cross-linking (formation of di-starch phosphate) with a general decrease in intensity, which is more obvious at the OH and C–OH bands, because of the interactions with the cross-linker [37]. The new peaks at 2,354.70, 1,218.02, and 840.22 cm\(^{-1}\) can be attributed to OH–P=O, P=O, and P–O–C stretching, respectively, at the points of cross-linking [38–40]. The PCCS spectra show that the carboxymethylation reaction further reduced the OH groups, as the intensity of the spectra further decreases. The sharpening and shifting of the peak to 1,723.00 cm\(^{-1}\) can be attributed to the overlap of the carbonyl (C=O) group, whereas the new peak at 1,489.43 cm\(^{-1}\) can be attributed to the carboxylate group (–COO\textsuperscript{−}/COONa) [36,38]. There are no SMCA characteristic peaks at 1,248 and 673 cm\(^{-1}\), showing that PCCS is free of residual SMCA [36]. Figure 2b shows the comparison of the FTIR spectra before (PCCS) and after the adsorption of Pb (PCCS-Pb) and Cd (PCCS-Cd). The disappearance of the bands at 2,354.70 cm\(^{-1}\) (O=PO–OH) and 847.22 cm\(^{-1}\) (P–O–C) indicated the involvement of the phosphoryl group in the adsorption of both ions. The reduction in OH band intensity was more after the adsorption of Cd\textsuperscript{2+} than Pb\textsuperscript{2+}, indicating that the OH groups are more involved in the adsorption of Cd\textsuperscript{2+} than Pb\textsuperscript{2+}. The band at 1,489.43 cm\(^{-1}\) (–COO\textsuperscript{−}/Na\textsuperscript{+}) shifted after the adsorption of Pb\textsuperscript{2+}, but this was not observed after the adsorption of Cd\textsuperscript{2+}. The reaction is illustrated in Scheme 1, and the proposed adsorption interaction is presented in Scheme 2. The dotted lines show the possible interactions of heavy metal ions with the PCCS derivatives.
Morphological characteristics. The SEM images of NS, PCS, PCCS, and ion-loaded derivatives (i.e., PCCS-Pb and PCCS-Cd) are presented in Figure 3. The surface of native starch granules (Figure 3a-a’) is smooth, and the granules have different sizes and shapes, such as round, oval, and spherical [41, 42]. The SEM images of PCS (Figure 3b-b’) show that cross-linking did not affect the granule structure; however, the surface of PCS granules looks slightly shinier than that of native starch granules. Hoover and Sosulski [28] also reported that cross-linking with low POCl₃ concentrations (0.05% to 0.50%) did not affect the granule structure of some...
Studies of the Removal of Pb\textsuperscript{2+} and Cd\textsuperscript{2+} from Aqueous Solutions

Scheme 1. Cross-linked Carboxymethyl Reaction Scheme

Scheme 2. Proposed Adsorption Interactions Between Heavy Metal Ion and PCCS
legume starches (e.g., lentil, faba bean, and field pea), which was attributed to the high amylose content of the starches and the rapid surface reaction by POCl₃. However, Singh and Nath [30] reported the increasing loss of structural integrity of moth bean starch granule as the POCl₃ concentrations in the reaction increased from 1.5% to 2.5%. The SEM images of PCCS (Figure 3c-c’) show slight fissures and distortions on the surface of the starch granule. This observation is similar to the reported increase in fissures on cross-linked mung bean starch granule as the amount of the carboxymethylating agent was increased [43]. This finding can be attributed to the defragmentation of the starch macromolecules at the surface of the granule as the bulky carboxymethyl group (–CH₂COONa) is substituted on the molecules. Figs. 3d-d’ and 3e-e’ show the SEM images of PCCS loaded with Pb²⁺ and Cd²⁺, respectively. The general observations include the disappearance of the fissures on the surface of the granule, the agglomeration of granules, and the partial fusion of granules. The disappearance of fissures was reported for cassava starch 5-chloromethyl-8-hydroxyquinoline hydrogel after the adsorption of Pb²⁺ and cross-linked potato starch xanthate after the adsorption of Pb²⁺ and Cd²⁺ [15, 32]. The agglomeration of granules was attributed to electronic interactions [44] because of the change in the amount of the cations and anions present in the granules after the adsorption process. The fusion of granules after adsorption was attributed to the swelling of the granules because of the metal ion interactions, and the material mass was associated with the exudation of starch–metal complexes, which are insoluble in aqueous solutions [15, 32, 45].

**Energy-Dispersive X-ray Spectroscopy.** Figure 4 shows the EDX spectra of NS, PCS, and PCCS. As expected for polysaccharides, the major peaks on the NS spectra (Figure 4a) are for carbon and oxygen (hydrogen is not detectable by EDX). The peak for phosphorous is also shown on the NS spectra, and this...
can be attributed to the phospholipids intrinsically present in the starch granules [46]. The PCS spectra (Figure 4b) show the sodium content and an increase in phosphorus content because of the phosphoryl groups, whereas the PCCS (Figure 4c) spectra show an increase in sodium content because of the sodium carboxymethyl group introduced into the starch molecules. Figs. 4d and 4e show the adsorption of heavy metal ions onto PCCS. The weight and atomic percentage data (wt% and at%) show higher adsorption of Pb$^{2+}$ than Cd$^{2+}$. The data also show that the adsorption of Pb$^{2+}$ was accompanied by a more significant reduction in Na content the adsorption of Cd$^{2+}$.

**Adsorption equilibrium.** The effect of pH on the adsorption of Pb and Cd on PCCS is presented in Figure 5a. The adsorption of Pb$^{2+}$ remains higher than that of Cd$^{2+}$. However, the adsorption of both ions increased with pH to the optimum pH of 6 and 7 for Pb and Cd, respectively, above which precipitation was observed. This finding is consistent with the optimum pH reported for the adsorption of Pb$^{2+}$ and Cd$^{2+}$ on sporopollenin [47]. At low pH, H$_3$O$^+$ competes for the active sites on the adsorbent and electrostatic repulsion occurs between metal ions and protonated sites [6], which can be attributed to the low adsorption of aqueous metal ions at low pH. The functional groups in the adsorbent and

![Figure 4. EDX Spectra with Elemental Data of (a) NS, (b) PCS, (c) PCCS, (d) PCCS-Pb, and (e) PCCS-Cd](image_url)
their tendency to protonate and deprotonate also determine the effects of pH on the adsorption capacity of such adsorbent [48]. Further studies were conducted at pH 6 for Pb²⁺ and pH 7 for Cd²⁺ to ensure equilibrium conditions.

The effect of time is presented in Figure 5b. Rapid adsorption onto PCCS occurred, and maximum adsorption was recorded for Pb²⁺ (99.10%) and Cd²⁺ (97.62%) within 5 min of interaction. Up to 240 min of interaction, the adsorption of aqueous ions onto PCCS was observed to intermittently increase and decrease as the contact time increases, as shown in Figure 5b. This dynamic equilibrium can be attributed to the subsequent desorption and re-adsorption of ions at interaction times beyond 5 min, which may be influenced by the partial solubilization of PCCS [8]. Compared with adsorption onto cross-linked carboxymethyl corn starch derivative (q time = 10 min), adsorption onto PCCS is more rapid [8]. This finding can be attributed to the intrinsic component(s) of starch and the surface area and crystallinity of its granules as differentiated botanically [17].

Figure 5c shows the effect of initial ion concentration on the adsorption of Pb²⁺ and Cd²⁺. PCCS derivatives exhibit appreciably higher adsorption capacity at low metal ion concentrations than some corn-starch-based adsorbents and other biosorbents [6, 48–50]. The highest adsorption was recorded at 100 ppm (99.44%) for Pb²⁺. Meanwhile, Cd²⁺ adsorption decreased (from 98.12% to 57x784]163  Akinterinwa, et al.  
Makara J. Sci.  
September 2020  |  Vol. 24  |  No. 3

Figure 5. Effect of (a) pH, (b) Contact Time, (c) Concentration, (d) Temperature, (e) Na⁺ and Ca²⁺ Concentrations, and (f) Adsorbent Dosage on the Adsorption of Pb²⁺ and Cd²⁺.
84.59%) above 50 ppm. This result showed that, although the adsorption sites on the PCCS derivatives are already saturated above 50 ppm for Cd$^{2+}$, adsorption continues for Pb$^{2+}$. This finding indicates the higher selectivity and availability of more adsorption sites for Pb$^{2+}$ than Cd$^{2+}$ on PCCS.

The effect of solution temperature is presented in Figure 5d, showing a gradual increase before the decline in adsorption capacity above 50 °C for both metal ions on PCCS. This finding can be attributed to distortions in the structure of starch granules at high temperatures. The decline in adsorption capacity above 60 °C was more rapid with Cd$^{2+}$, which can be attributed to the difficult formation and/or easy breakage of van der Waals forces that seem to be more involved in the adsorption of Cd$^{2+}$.

Figure 5e shows the ionic interference in the adsorption of Pb$^{2+}$ and Cd$^{2+}$ onto PCCS in aqueous solutions containing Na$^+$ and Ca$^{2+}$. Ionic interference is due to competitions for active sites on a adsorbent. Na$^+$ reduces the adsorption of Cd$^{2+}$ more than Pb$^{2+}$, whereas Ca$^{2+}$ reduces the adsorption of Pb$^{2+}$ more than Cd$^{2+}$. This finding indicates that Ca$^{2+}$ competes more than Na$^+$ for adsorption sites with a high affinity for Pb$^{2+}$.

The effect of PCCS dosage is presented in Figure 5f. The adsorption capacity of PCCS increases with the increase in the adsorbent dosage because of the increase in adsorption sites. Nearly complete removal of the metal ions (99.92% for Pb$^{2+}$ and 99.76% for Cd$^{2+}$) was recorded at 3% PCCS dosage.

### Adsorption kinetics

The adsorption data were evaluated using the linearized Lagergren’s pseudo-first-order model (Eq. 5) [6]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t,$$

where $k_1$ (min$^{-1}$) is the rate constant, $q_t$ (mg/g) is the amount of adsorbent on adsorbent at time $t$ (min), and $q_e$ (mg/g) is the amount of adsorbate on adsorbent at equilibrium. $k_1$ is obtained from the slope of the plot of $\ln(q_e - q_t)$ against $t$ (Figure 6a). The calculated $R^2$ and $q_e$ (Table 2) indicated that the Cd$^{2+}$ data fit the model better than the Pb$^{2+}$ data. This finding infers that the physiosorption mechanism is more involved in the adsorption of Cd$^{2+}$ than Pb$^{2+}$.

The linearized expression for the pseudo-second-order model is given in Eq. 6 [24]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e},$$

where $k_2$ (g·mg$^{-1}$·min$^{-1}$) is the rate constant, $q_t$ (mg/g) is the amount of adsorbate on adsorbent at time $t$ (min), and $q_e$ (mg/g) is the amount of adsorbate on adsorbent at equilibrium. The adsorption data are evaluated by plotting $t/q_t$ against $t$ (Figure 6b). The $R^2$ and $q_e$ values (Table 2) show that the Pb$^{2+}$ data fit the model better than the Cd$^{2+}$ data. This finding indicates that the chemisorption mechanism is more involved in the removal of Pb than Cd [51].

The adsorption data were evaluated by the intraparticle diffusion model (Eq. 7) [25]:

$$q_t = K_{id} t^{1/2} + l,$$

where $K_{id}$ (mg·g$^{-1}$·min$^{-1/2}$) is the intraparticle diffusion rate constant and $l$ (mg/g) is the estimated layer boundary thickness. $K_{id}$ and $l$ are obtained from the slope and intercept of the plot of $q_t$ against $t^{1/2}$, respectively (Figure 6c). Data points on the graph can be related to two straight lines. The initial shorter line denotes macropore diffusion (outside the granules), indicating that macropore diffusion is insignificant. The final line denotes mesopore diffusion (within the granules). Intraparticle diffusion cannot be said to be involved in the rate-determining steps of the overall process because the curves are far from the origin and the $R^2$ values are far from unity, which may be attributed to the high concentrations of adsorption sites on the surface than the bulk of the adsorbent.

The fitness of the adsorption data to the external diffusion model indicates that the diffusion of metal ions through the fuse layer coating the adsorbent is the rate-determining step, which is typical when the active sites are concentrated at the surface (beneath the fuse layers). The expressions for the model are given in Eqs. 8 and 9 [26]:

$$\ln \left[\frac{1}{1 - F(t)}\right] = K_{ed} t,$$

where $F(t)$ is the fractional attainment of equilibrium at time $t$ and $K_{ed}$ (min$^{-1}$) is the effective diffusion coefficient of the adsorbate in the adsorbent phase. $K_{ed}$ was obtained from the slope of the plot of $\ln(1/[1 - F(t)^2])$ against $t$ (Figure 6d). The $R^2$ values (Table 2) obtained for both metal ions are close to unity, indicating that the rate of diffusion through the fuse layers is important in the rate-determining steps of the process.
Figure 6. Plot and Parameters of the (a) Pseudo-first-order, (b) Pseudo-second-order, (c) Intraparticle Diffusion, and (d) External Diffusion Models

Table 2. Kinetic Parameters of the Adsorption of Pb\(^{2+}\) and Cd\(^{2+}\) Ions onto PCCS Derivatives

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pb (II)</th>
<th>Cd (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experiment</strong></td>
<td>4.960</td>
<td>4.880</td>
</tr>
<tr>
<td><strong>Pseudo-first Order</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(q_{e,cal} (\text{mg g}^{-1}))</td>
<td>4.0601</td>
<td>4.8472</td>
</tr>
<tr>
<td>(k_1 (\text{min}^{-1}))</td>
<td>1.5723</td>
<td>1.7076</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.9767</td>
<td>0.9976</td>
</tr>
<tr>
<td><strong>Pseudo-second Order</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(q_{e,cal} (\text{mg g}^{-1}))</td>
<td>4.7393</td>
<td>3.9262</td>
</tr>
<tr>
<td>(k_2 (\text{g mg}^{-1} \text{ min}^{-1}))</td>
<td>7.9503</td>
<td>4.2125</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.9999</td>
<td>0.9976</td>
</tr>
<tr>
<td><strong>Intra-particle diffusion</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k_{id} (\text{mg g}^{-1}))</td>
<td>0.3618</td>
<td>0.4559</td>
</tr>
<tr>
<td>(I)</td>
<td>3.7400</td>
<td>3.3450</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.6541</td>
<td>0.6482</td>
</tr>
<tr>
<td><strong>External diffusion</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(K_{ed} (\text{min}^{-1}))</td>
<td>1.4643</td>
<td>1.6245</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.9792</td>
<td>0.9823</td>
</tr>
</tbody>
</table>

Adsorption isotherms. The adsorption data were evaluated using the Langmuir adsorption isotherm model, and its linearized equation is given in Eq. 10 [6]:

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m},
\]

where \(q_e\) (mg/g) is the amount of adsorbate on the adsorbent; \(C_e\) (mg/L) is the adsorbate concentration in solution at equilibrium; \(K_L\) (L/mg) is the Langmuir constant, which correlates with the variation in the active surface area and porosity on the adsorbent; and \(q_m\) (mg/g) is the maximum adsorption capacity of the monolayer formed on the adsorbent. \(K_L\) and \(q_m\) are calculated from the intercept and slope of the plot of \(C_e/q_e\) against \(C_e\), respectively (Figure 7a). The \(R^2\) and \(q_m\) values (Table 3) show that the Pb data fit the Langmuir model better than the Cd data, indicating the involvement of the chemisorption mechanism. The separation factor \(R_L\) given in Eq. 11 indicates a favorable adsorption process, i.e., \(0 < R_L < 1\), for both ions [6]:

\[
R_L = \frac{1}{1 + K_L C_0}.
\]

The linearized equation representing the Freundlich isotherm model is given in Eq. 12 [6]:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e.
\]
where $K_F$ is the adsorption capacity (L/mg) and $1/n$ defines the adsorption intensity and relative distribution of energy and the heterogeneity of the adsorbate sites. $n$ values between 1 and 10 indicate a favorable adsorption process. $K_F$ and $1/n$ are obtained from the intercept and slope of the plot of $\log q_e$ against $\log C_e$, respectively (Figure 7b). The parameters listed in Table 3 show that the Cd data fit the Freundlich model better than the Pb data, with a more favorable adsorption process ($n$ value is farther from the lower limit).

The Temkin isotherm model takes into account the effects of indirect adsorbent/adsorbate interactions on the adsorption process. The linearized equation is expressed as Eq. 13 [27]:

$$q_e = B \ln K_T + B \ln C_e,$$

where $K_T$ (L·g$^{-1}$) is the Temkin isotherm constant corresponding to the maximum binding energy and $B$ (J/mol) is the Temkin constant related to the heat of adsorption, i.e., $B = RTb$, where $R$ is the gas constant (8.314 J/mol K) and $T$ (K) is the absolute temperature. $B$ and $K_T$ are obtained from the slope and intercept of the plot of $q_e$ against $\ln C_e$, respectively (Figure 7c). Table 3 shows that the $R^2$ value of Pb is closer to unity than that of Cd. Moreover, the Temkin constants related to maximum binding energy and heat of adsorption are higher for Pb$^{2+}$ than Cd$^{2+}$, indicating the higher affinity of the adsorbent for Pb$^{2+}$ than Cd$^{2+}$. A similar evaluation has been reported for the adsorption of Pb$^{2+}$ on biomass substituted with carbonyl groups [27].

**Thermodynamic studies.** To analyze the thermodynamic parameters of the effect of temperature on the adsorption of metal ions, the van’t Hoff’s equation given in Eq. 14 was used [52]:

$$\log K_e = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT},$$

where $K_e$ (equilibrium constant) = $Q/C_e$ (where $Q$ (mg/g) is the equilibrium solid-phase concentration and $C_e$ (mg/L) is the equilibrium solution concentration), $R$ = 8.314 J·mol$^{-1}$·K$^{-1}$ is the gas constant, $T$ (K) is the temperature, $\Delta S$ is the entropy, and $\Delta H$ is the enthalpy.

Figure 7. Plot and Parameters of the (a) Langmuir, (b) Freundlich, and (c) Temkin Isotherm Models
\( \Delta S \) and \( \Delta H \) are obtained by calculation using the intercept and slope of the van’t Hoff plot of \( \log K_c \) against \( 1/T \) (Figure 8). Free energy (\( \Delta G \)) was calculated using the thermodynamic equation given in Eq. 15:

\[
\Delta G = \Delta H - T \Delta S.
\] (15)

As shown in Table 4, the negative values obtained for \( \Delta H \) indicate that the overall process is exothermic. The negative values of \( \Delta G \) indicate that the adsorption process is feasible and spontaneous. The negative values of \( \Delta G \) decreased as the temperature increased. This showed that the adsorption process becomes less feasible and spontaneous as the temperature increased. The values of the thermodynamic parameters also indicate that the adsorption process of the two metal ions includes both physisorption and chemisorption mechanisms. However, physisorption dominates in the adsorption of \( \text{Cd}^{2+} \) [52].

**Desorption/regeneration and reusability studies.** To evaluate the economical utilization of PCCS derivatives and avoid the return of heavy metals back to the environment upon disposal of the adsorbant, the recovery of the sorbed metal ions was investigated using \( \text{HNO}_3 \) (Figure 9a). A fast and approximately 100% recovery was obtained for heavy metal ions. The faster recovery of \( \text{Cd}^{2+} \) than \( \text{Pb}^{2+} \) can be attributed to the predominant physisorption mechanism during its adsorption process. The results recorded for \( \text{Pb}^{2+} \) is better than those recorded for succinylated corn starch reported in [50]. Fig. 9b shows the cycles of regeneration and reuse of PCCS. In the first three cycles, adsorption remains above 80% for both ions. The reduction in adsorption capacity has been attributed to the gradual dissolution and degradation of the derivative during the cycles of regeneration and reuse [8]. The reduction in adsorption may also be attributed to incomplete deprotonation after the desorption process.

**Table 3. Isotherm Parameters of Adsorption onto PCCS Derivatives**

<table>
<thead>
<tr>
<th>Isotherm Model</th>
<th>Parameters</th>
<th>( \text{Pb}^{2+} )</th>
<th>( \text{Cd}^{2+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment Langmuir</td>
<td>( q_m ) (mg/g)</td>
<td>19.6950</td>
<td>16.2560</td>
</tr>
<tr>
<td></td>
<td>( k_L ) (L/mg)</td>
<td>0.9125</td>
<td>0.2281</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.9989</td>
<td>0.9692</td>
</tr>
<tr>
<td></td>
<td>( R_1 ) (L/mg.L^-1)</td>
<td>0.3248</td>
<td>0.4672</td>
</tr>
<tr>
<td></td>
<td>( R_2 )</td>
<td>0.1939</td>
<td>0.3045</td>
</tr>
<tr>
<td></td>
<td>( R_3 )</td>
<td>0.0742</td>
<td>0.1275</td>
</tr>
<tr>
<td></td>
<td>( R_4 )</td>
<td>0.0119</td>
<td>0.0215</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( k_f ) (L/mg) ( 1/n )</td>
<td>10.3538</td>
<td>3.6091</td>
</tr>
<tr>
<td></td>
<td>( l/h )</td>
<td>0.7900</td>
<td>0.3776</td>
</tr>
<tr>
<td></td>
<td>( n )</td>
<td>1.2658</td>
<td>2.6483</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.9604</td>
<td>0.9689</td>
</tr>
<tr>
<td>Temkin</td>
<td>( R^2 )</td>
<td>4.9555</td>
<td>2.7273</td>
</tr>
<tr>
<td></td>
<td>( k_f ) (L/mg)</td>
<td>11.0470</td>
<td>3.9623</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.9462</td>
<td>0.9205</td>
</tr>
</tbody>
</table>

**Table 4. Thermodynamic Parameters of the Removal of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) Ions using PCCS Derivatives**

<table>
<thead>
<tr>
<th>Metal Ions</th>
<th>T (K)</th>
<th>( \Delta G ) (kJmol(^{-1}))</th>
<th>( \Delta H ) (kJmol(^{-1}))</th>
<th>( \Delta S ) (Jmol(^{-1})K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pb}^{2+} )</td>
<td>303</td>
<td>-5.93</td>
<td>-15.51</td>
<td>-31.61</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-6.12</td>
<td>-15.51</td>
<td>-31.61</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-6.30</td>
<td>-15.51</td>
<td>-31.61</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>-4.98</td>
<td>-15.51</td>
<td>-31.61</td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>-4.67</td>
<td>-15.51</td>
<td>-31.61</td>
</tr>
<tr>
<td>( \text{Cd}^{2+} )</td>
<td>303</td>
<td>-6.08</td>
<td>-9.79</td>
<td>-12.24</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-5.96</td>
<td>-9.79</td>
<td>-12.24</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-5.84</td>
<td>-9.79</td>
<td>-12.24</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>-5.71</td>
<td>-9.79</td>
<td>-12.24</td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>-5.59</td>
<td>-9.79</td>
<td>-12.24</td>
</tr>
</tbody>
</table>
PCCS comparison and practical application. The derivative used in this study was compared with other starch derivatives (Table 5). The rate of adsorption is rapid and can only be compared to that of Chen et al. [44]. Even with less carboxymethylating agent used (as selected for legume starch), the adsorption capacity of the material used in this study is competitive with those investigated by Kim and Lim [8] and better than those of Zdanowicz et al. [53]. Materials with higher adsorption capacities than PCCS (as shown in Table 5)

![Figure 8. Plot of logKc against 1/T for the Adsorption of Pb$^{2+}$ using PCCS-15% and Cd$^{2+}$ using PCCS-5%](image)

![Figure 9. (a) Desorption and Recovery of Pb$^{2+}$ and Cd$^{2+}$ and (b) Reusability of PCCS](image)

Table 5. Comparison of the Adsorption Efficiency of PCCS with other Reported Starch Derivatives

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dose (%w/v)</th>
<th>Pb$^{2+}$</th>
<th>Cd$^{2+}$</th>
<th>Pb$^{2+}$</th>
<th>Cd$^{2+}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>POCl3 cross-linked carboxymethyl corn starch</td>
<td>1</td>
<td>203</td>
<td>194</td>
<td>20.25*; 10</td>
<td>19.37*; 10</td>
<td>[8]</td>
</tr>
<tr>
<td>Dichloroacetic acid cross-linked carboxymethyl potato starch</td>
<td>1</td>
<td>116.8</td>
<td>102.0</td>
<td>11.65; 45</td>
<td>10.18; 45</td>
<td>[53]</td>
</tr>
<tr>
<td>Succinylated tapioca starch microcrystal</td>
<td>0.2</td>
<td>100</td>
<td>100</td>
<td>32.4; 5</td>
<td>26.8; 5</td>
<td>[44]</td>
</tr>
<tr>
<td>Cross-linked potato starch xanthate</td>
<td>0.02</td>
<td>10</td>
<td>10</td>
<td>47.1; 240</td>
<td>36.55; 240</td>
<td>[15]</td>
</tr>
<tr>
<td>Succinylated corn starch microcrystal</td>
<td>0.2</td>
<td>100</td>
<td>-</td>
<td>6.91; 90</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>Corn starch phosphate carbamates</td>
<td>0.1</td>
<td>621*</td>
<td>-</td>
<td>416.1*; 20</td>
<td>-</td>
<td>[9]</td>
</tr>
<tr>
<td>Dithiocarbamate (DTC)-modified corn starch</td>
<td>0.01</td>
<td>100</td>
<td>-</td>
<td>260.82*; 720</td>
<td>-</td>
<td>[4]</td>
</tr>
<tr>
<td>Carboxymethyl cross-linked amphoteric corn starch</td>
<td>0.08</td>
<td>70</td>
<td>-</td>
<td>152.74; 60</td>
<td>-</td>
<td>[49]</td>
</tr>
<tr>
<td>Maize starch-g-poly(N-vinylimidazole)</td>
<td>0.2</td>
<td>-</td>
<td>22.4</td>
<td>-</td>
<td>36.18; 1440</td>
<td>[14]</td>
</tr>
<tr>
<td>POCl3 cross-linked carboxymethyl legume starch</td>
<td>1</td>
<td>200</td>
<td>200</td>
<td>19.70; 5</td>
<td>16.26; 5</td>
<td>This Work</td>
</tr>
</tbody>
</table>

Key: * = converted from the concentration presented in the literature.

Table 6. Removal of Heavy Metals from Wastewater using 1% (w/v) of PCCS-5% (pH Adjusted to 6; Adsorption Time = 5 min)

<table>
<thead>
<tr>
<th>Elements</th>
<th>C0</th>
<th>C1</th>
<th>C0</th>
<th>C1</th>
<th>Inland discharge compliance limits maximum in ppm [54]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>1.8218</td>
<td>0.0403 ± 0.0002</td>
<td>0.9293</td>
<td>ND</td>
<td>0.05</td>
</tr>
<tr>
<td>Cd</td>
<td>0.6246</td>
<td>ND</td>
<td>1.4967</td>
<td>ND</td>
<td>No limit</td>
</tr>
<tr>
<td>Cr (total)</td>
<td>0.4367</td>
<td>ND</td>
<td>0.6218</td>
<td>ND</td>
<td>0.3000</td>
</tr>
<tr>
<td>Zn</td>
<td>0.0315</td>
<td>ND</td>
<td>0.8050</td>
<td>ND</td>
<td>1.000</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0561</td>
<td>ND</td>
<td>2.0693</td>
<td>ND</td>
<td>1.500</td>
</tr>
<tr>
<td>Fe</td>
<td>2.4534</td>
<td>ND</td>
<td>3.3956</td>
<td>ND</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Key: Sample A = wastewater from gold processing site; Sample B = wastewater from crude oil exploration; C0 = initial concentration; C1 = final concentration; ND = not detected (absent or lower than the limit of detection, i.e., Pb = 0.04 ppm, Cd = 0.02 ppm, Cr = 0.04 ppm, Zn = 0.02 ppm, Cu = 0.02 ppm, and Fe = 0.03 ppm); C1 data were presented as the mean ± SD of triplicate analysis.
are also more expensive, considering the production processes. Therefore, they may not be cost-efficient for practical applications.

Table 6 present the results from practical applications of PCCS to the removal of heavy metals from different wastewater samples. Notably, the matrix of the wastewater samples may contain more varieties of cations than the ones listed in Table 6. Pb and Cd, as well as other heavy metal ions, analyzed in the wastewater samples can be said to have been reduced to acceptable levels according to the inland discharge compliance limit of the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria.

**Conclusion**

Legume starches are higher amylose and higher crystallinity starches. This study has shown that these properties may have transcended to the adsorption potentials of their derivatives. The characterization of native starch and its derivatives indicated a successful modification. PCS and PCCS derivatives showed adsorption capability for both Pb²⁺ and Cd²⁺; however, PCCS showed higher adsorption characteristics than PCS. The adsorption process can be described as a combination of physisorption and chemisorption mechanisms, which include the trapping of ions in the polymer matrix, electrostatic interactions, ion exchange, and chelation. The adsorption of Pb²⁺ onto PCCS is higher than that of Cd²⁺. Hence, the mechanisms involved in the adsorption of Pb and Cd cannot be regarded to be the same. Sodium ion exchange was determined to be involved in the adsorption process of Pb²⁺. Meanwhile, electrostatic interactions enhanced by nonbonded hydroxyl groups were involved in the adsorption process of Cd²⁺. Ion fixation on PCCS was rapid (qt, time = 5 min). The kinetic parameter of Pb²⁺ fitted the pseudo-second-order model better, while Cd²⁺ fitted pseudo-first-order model better. The adsorption isotherm parameters of Pb²⁺ fitted the Freundlich and Temkin isotherm models better than that of Cd²⁺, while Cd²⁺ fitted the Langmuir isotherm model better than that of Pb²⁺. These indicated different dominant mechanisms in the adsorption of the two ions. Excellent recovery of metal ions was achieved. However, PCCS could only maintain its efficiency (>80%) up to the third reuse cycle. Practical applications show that PCCS could be a versatile heavy metal adsorbent.

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