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Preparation and characterization of succinylated starch as adsorbent for the removal of Pb (II) ions from aqueous media

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Abstract: *Succinylation of corn starch to high degree of substitution (DS) was studied by reacting starch with succinic anhydride. The synthesized sorbent (SCSs) with different DS (0.19, 028 and 0.47) were used as an adsorbent for the removal of Pb (II) ions from aqueous media. SCS was characterized by Fourier transform infrafed spectroscopy (FTIR), Scanning electron microscopy (SEM), Thermogravimetry (TG), Brunauer-Emmett-Teller (BET). The results of FTIR showed the difference between native corn starch (NCS) and SCS in the spectrum. Batch adsorption experiments were carried out as a function of pH and initial Pb (II) ions concentration. The adsorption results revealed that the optimal pH was 6.0, the equilibrium time was about 90 min. ICP-OES analysis revealed that when the initial Pb(II) ion concentration was increased from 20 mg/L up to 100 mg/L, the adsorption capacity of SCS1, SCS2, and SCS3 increased from 1.502 to 4.421 mg/g, 1.911 to 5.812 mg/g, and 2.114 to 6.910 mg/g, respectively. The SCS3 adsorption capacity was much better than others. The adsorption follows the Langmuir isotherm and the adsorption capacity increases with the increasing of DS of the SCS. Furthermore, the SCS showed the advantage of good reusability and high desorption efficiency.*

Keywords: *Succinic anhydride, Modified starch, Adsorption, Pb (II), Langmuir constant*

I. Introduction

Toxic heavy metals in air, soil, and water are global problems that are a growing threat to humanity. There are hundreds of sources of heavy metal pollution, including the coal, natural gas, paper, and chloro-alkali industries [1-2]. Under the current regulations in most countries, industries are obligated to treat wastewater and to reduce toxic metal concentration to less than certain designated values [3]. The removal of heavy metal ions from aqueous media has been conventionally carried out by several techniques such as reverse osmosis, adsorption, ion exchange, complexation and precipitation. The use of synthetic resins for chelating toxic metal ions in wastewater is a possible approach for preventing environmental pollution and recycling metals. These resins are mostly composed of petroleum-based synthetic polymers [4-6]. In general, after the adsorption process for metal ions, the chelating resins are discarded in landfills or treated by incineration. Nonetheless, these processes often result in secondary environmental pollution by contaminating the soil or air, because, these synthetic polymers are usually non-renewable and non-biodegradable.

Starch, an agricultural biopolymer, is more attractive for industrial use because of its renewability, biodegradability, and low unit cost. However, starch by itself could not be suitably applied in chelating or adsorbing heavy metal ions to replace the synthetic chelate resins, because it has naturally no chelating or metal-interaction capacity. Hence, several approaches have been made to utilize starch as a metal scavenger, by introducing the substituents of chelating activity, such as acrylamide and tertiary amine phosphate groups [7-8]. Among the various starch derivatives, starch substituted with a carboxyl group such as maleic acid has been used as a thickening or stabilizing agent in soup, snack and frozen food products [9]. However, little is known about the metal-binding properties of these anionic starches.

Therefore, the objective of this study is to prepare a succinylated corn starch (SCS) having different degrees of substitution and use it to remove Pb(II) ions from aqueous media.

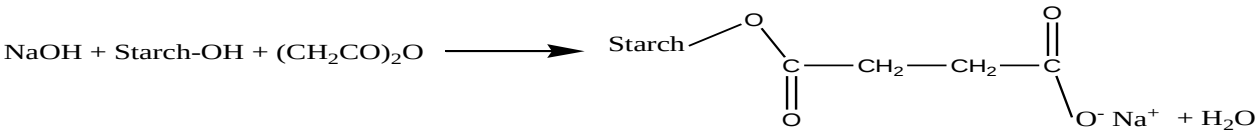
II. Materials And Methods

2.1. Materials

Corn starch (food grade) was dried at 105 ^{0}C before it was used. Succinic anhydride was purchased from Sigma Aldrich (Johannesburg, South Africa) and used as obtained. All the chemicals used were of analytical grade.

2.2. Preparation of succinylated starch

The method of sathe and salunkhe [10] was used. Starch (100g) was dispersed in 300 ml of distilled water and stirred magnetically for 1 h. The pH of the slurry was adjusted to pH 9.0 using 1 M NaOH. Different amount of succinic anhydride (5, 10 and 15 g) were used to treat the starch suspension (to obtain starch succinate of three different degrees of substitution) over a period of 2 h while maintaining a pH range of 8.0 – 9.0. At the end of the reaction the pH of the slurry was adjusted to pH 6.0 using 0.5 M HCl. The mixture was filtered, and the modified starch washed six times with distilled water and oven dried for 24 h at 50 ^{0}C.



Scheme 1. Synthesis of Starch Succinate

2.3. Determination of degree of modification

The method of alkali sapanification as described by Genung and Mallatt [11] was employed for the determination of succinyl content. A sample (1 g) was weighed into a conical flask, 50 mL of 75% EtOH was added, and the mixture was refluxed for 30min while maintaining a temperature of 50^{0}C. After cooling to room temperature, 40 mL of 0.5 M NaOH was added. The flask was covered with aluminium foil and allowed to stand at room temperature for 72 h with occasional shaking. Saponification occurred with the addition of NaOH, and the excess alkali was determined by titrating with 0.5M HCl using phenolphthalein indicator. Native starch was treated in the same manner to obtain a value for the blank. The percentage of succinyl group and the degree of substitution of the samples calculated using Eqn 1and 2 respectively.

$$\% \text{ Succinyl} = \frac{(\text{Blank titre} - \text{sample tire}) \times 0.1 \times \text{molarity of acid} \times 100}{\text{Weight of the sample}} \qquad 1$$

$$\text{Degree of substitution (DS)} = \frac{162 \times \% \text{ succinyl}}{1000 - (99 \times \% \text{ succinyl})} \qquad 2$$

2.4. Scanning Electron Microscopy (SEM)

To determine the surface morphology of the native and succinylated starches, the starches were taken and dusted onto a carbon sticker, then coated with gold using a sputter coater (Balzers Union, FL-9496) for 30 min. Images were recorded using INCAPentaFETx3 (Vega Tescan) SEM fitted with an Oxford ISIS EDS.

2.5. FT-IR Spectroscopy

The Fourier transform infrared (FT-IR) spectra of native and succinylated starches were obtained using a PerkinElmer Spectrum 100 FT-IR spectrometer with an AutoIMAGE System.

2.6. Thermogravimetric Analysis (TGA)

Approximately 2 mg of the starch was placed in an open aluminium pan. The sample was heated at a heating rate of 10 ^{0}C min^{-1} from 45 ^{0}C to 650 ^{0}C temperature range under nitrogen atmosphere (flow rate = 20 mL min^{-1}) using a TGA 7 Perkin Elmer (System 2000 TG-IR).

2.6 Surface Area Analysis

Gas adsorption analysis was carried out using a Micromeritics ASAP 2020 Accelerated Surface Area and Porosity Analyser (DuPont, USA). The samples were first degassed at 105 ^{0}C under vacuum overnight to remove any adsorbed solvent. The adsorption isotherm of these degassed samples were then measured using nitrogen as the adsorbate at a temperature of 180 ^{0}C and specific surface areas were derived from N_2 gas adsorption-desorption isotherms (p/p_0 = 0.05–0.20).

2.7 Adsorption Experiments

The adsorption of lead(II) ions on SCS was studied by batch technique. It was performed at room temperature by adding an optimal quantity of the succinylated starch (100 mg) into 50 mL of a $Pb(NO_3)_2$ aqueous solution with initial concentrations ranging from 20 to 100 mg/L. The initial pH was adjusted with 0.1 M HNO_3 or 0.1 M NaOH before adding the adsorbent. After shaking for 90 min to ensure full equilibration, the mixture was centrifuged at 12 000 rpm for 5 min, and the final concentration of lead(II) was determined by ICP-OES.

The adsorption quantity (Q_e, mg/g) was calculated before and after the adsorption according to the eqn 3;

$$Q_e = \frac{V(Co - Ce)}{M} \quad (3)$$

where C_0 is the initial lead(II) ions concentration (mg/L), C_e is the lead(II) ions concentration at adsorption equilibrium (mg/L), V is the volume of lead(II) ions solution (L), and M is the weight of the adsorbent (g). The adsorption capacity values was evaluated using Langmuir equation (eqn 4)[12];

$$\frac{Ce}{Qe} = \frac{Ce}{Qm} + \frac{1}{(Ka\,Qm)} \quad (4)$$

where C_e (mg/L) and Q_e (mg/g) are lead(II) ions concentration and adsorption amount at adsorption equilibrium, Q_m (mg/g) and K_a (L/mg) are the theoretical maximum adsorption capacity and Langmuir equilibrium constant related to the theoretical maximum adsorption capacity and energy of adsorption, respectively.

2.8. Desorption Experiments

In order to determine the reusability of the SCS, the adsorption-desorption process was repeated four times. The lead(II) ions SCS loaded adsorbent was put into 100 mL of 1% (v/v) HNO_3 solution for 30 min at room temperature. The desorption efficiency (DE) was calculated according to eqn (5):

$$DE = \frac{C_t V}{M_o} \times 100\% \quad (5)$$

where C_t (mg/L) is the concentration of Pb (II) ions in the desorption solution at time t (min), V is the volume of the desorption, and M_o (g) is the amount of Pb (II) ions adsorbed.

III. Results And Discussion

3.1. Degree of succinylation

The reaction process of SCS can be proposed as Scheme 1. The results of the degree of substitution for SCS showing % succinyl groups are presented in Table 1. Three kinds of SCS were designated as SCS1, SCS2 and SCS3, of which the degree of succinylation could be controlled by the addition of succinic anhydride (5, 10 and 15 g), respectively. The DS value and % succinylation increased with increase in concentration of succinic anhydride, and thus, suggests that increase in concentration of succinic anhydride favours the production of starch succinate.

Table 1
Degree of substitution for SCS showing % succinyl groups

Sample	% Succinyl	DS	BET (m^2/g)
SCS1	0.95	0.19	22.6
SCS2	1.38	0.28	25.9
SCS3	2.25	0.47	28.4
NCS	-	-	17.8

3.2. Characterization of the prepared SCS

3.2.1 Surface morphology of SCS and NCS

Scanning electron micrographs of native corn starch (NCS), and representative of SCS were shown in Figure 1. It can be seen that the surface of the NCS particles were smooth, however, the particles of SCS appear obviously diverse. Evidently, there are particle fragments and irregular structure on the surface. Such cracks and irregularities are gainful for the metal ions to diffuse to the adsorption sites located in the inner portion of the adsorbent [13].

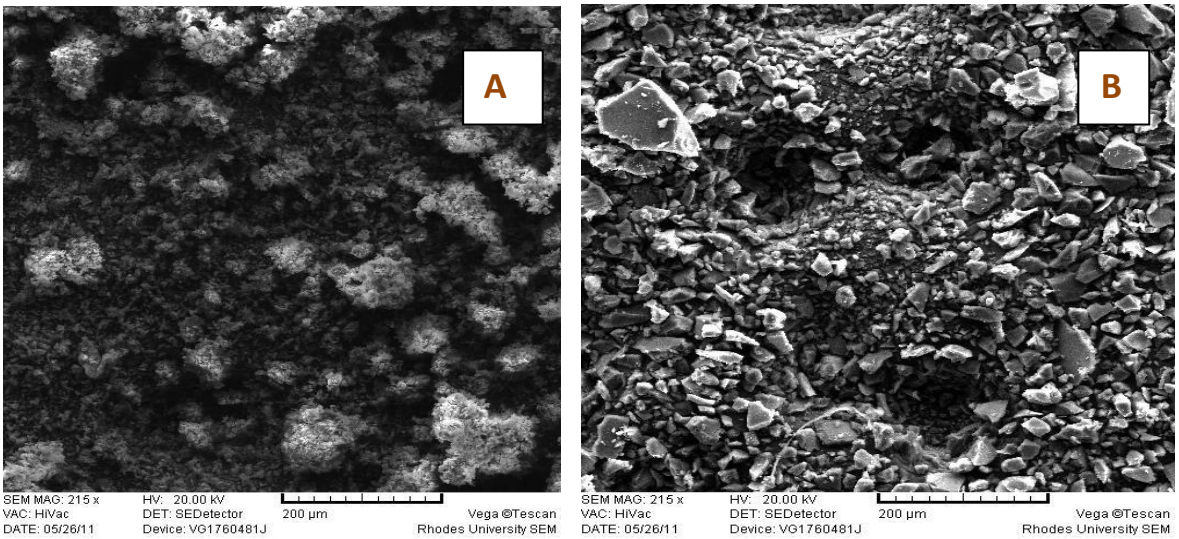


Fig. 1 **(A)** The scanning electron micrographs of SCS3, and **(B)** NCS

3.2.2. The FT-IR spectra of SCS and NCS

The infrared spectra of the compounds under investigation were recorded in the 4000–650 cm^{-1} region. As shown in Figure 2, the broad band between 3100 cm^{-1} and 3000 cm^{-1} is assigned to O-H stretching and it is due to hydrogen bonding involving the hydroxyl groups on the starch molecules. On succinylation, the FT-IR showed a new peak around 1733 cm^{-1} for the carboxylic acids of succinate group.

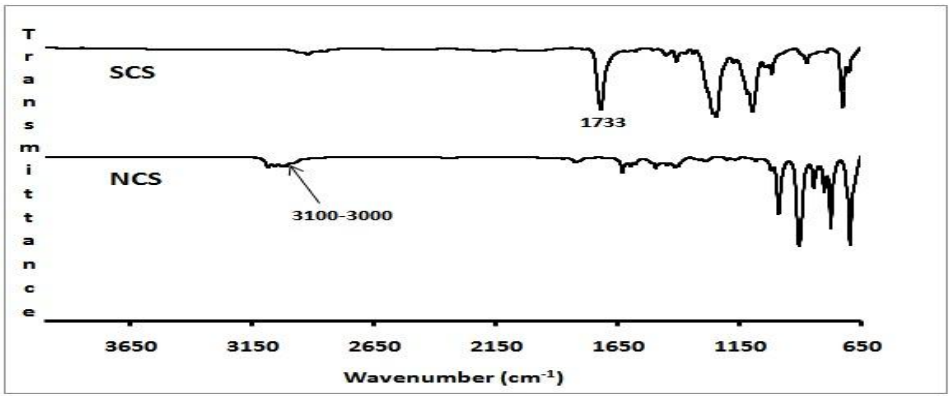


Fig. 2. FT-IR spectra SCS and NCS

3.2.3. BET– Specific surface area

Specific surface area is a material property that has a particular importance in case of adsorption, heterogeneous catalysis and reactions on surfaces. The BET surface area analysis data, which is also listed in Table 1, shows that adding varying amounts of succinic anhydride as a chelator to NCS has a significant effect on the specific surface area of the produced SCS and cause it to be increased from 17.8 to 22.6, 25.9, and 28.4 m^2g^{-1}, respectively. Besides, the specific surface area increased with the raise of DS.

3.2.4. Thermal stability analysis

Thermogravimetry analyses (TGA) curves were employed to examine the change of thermal stability caused by the succinylation. Figure 3 shows TGA curves of NCS and starch succinates (SCSs). Degradation of NCS starch began at 370 ^oC and ended at 440 ^oC with about 80.2% weight loss. Continuous heating to 640 ^oC resulted in ash formation [14]. For starch succinates, when the DS value was 0.19, degradation was similar to that of NCS with lower weight losses. When DS increased to 0.28, thermal stability increased noticeably and the thermal degradation took place at 420 ^oC. When DS increased to 0.47, thermal degradation occurred at 440 ^oC, 20 ^oC higher than that of DS 0.28. The increase in thermal stability with increasing DS was attributed to a small

number of hydroxyl groups remaining after succinylation. Thus, a high DS had a beneficial effect on the thermal stability of the sample.

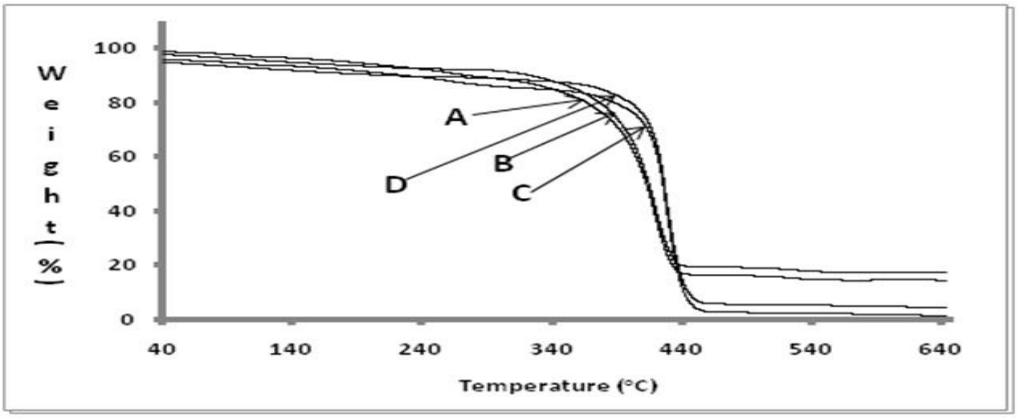


Fig.3. Thermogravimetry analysis (TGA) curves of native NCS (A) and starch succinates with DS values of 0.19 (B), 0.28 (C), and 0.47 (D).

3.3. Adsorption of Pb^{2+} ions

3.3.1. Effect of initial pH

The solution pH plays an important role in adsorption process [15]. Hence, the metal adsorption capacity of the anionic SCS sorbents were examined at different pHs of the metal solutions. The results in Fig. 4 showed that the adsorption capacities increase with the increase of pH. Negligible adsorption could be found at a lower pH range of 2.0 –4.0. The adsorption then increased gradually with pH increasing from 5.0 to 6.0. This might be due to the fact that the adsorbents were highly protonated in an acid medium, and cannot effectively interact with the metal ions because of the loss of negative charge [16]. Thus, the increased proton concentration in the medium inhibited the metal-chelate complex of the adsorbent. The increase in lead (II) adsorption at higher pH values (5.0–6.0) may be explained by the ionization of the reaction sites on the chelate surface which involves competitive reactions of protonation and complex binding [17]. A decrease in the adsorption of lead (II) ions was noticed above pH 6. All the three kinds of SCS have the same trends, and their adsorption capacities increase with the increase of DS in the same pH, i.e SCS1 < SCS2 < SCS3. For all subsequent experiments, the optimum pH value was used.

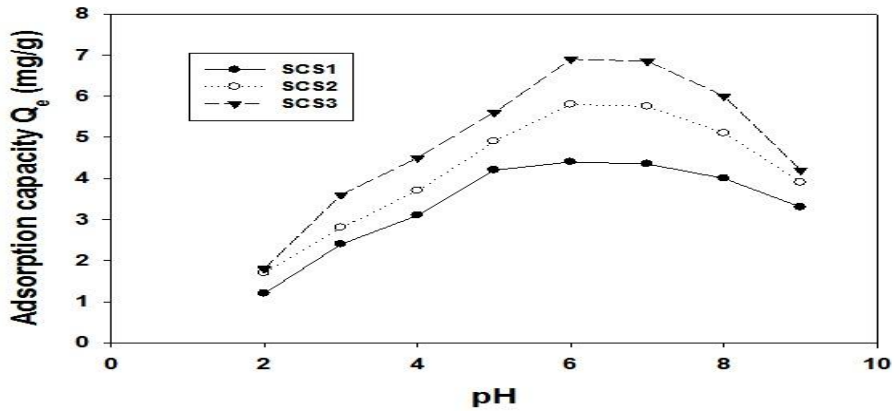


Fig.4. Effect of pH of Pb (II) ions adsorption on the SCS adsorbents

3.3.2 Effect of the initial Pb(II) ions concentration

In order to determine the adsorption strength of the SCS adsorbent for Lead adsorption, the effect of initial concentrations of Pb(II) ions was investigated by varying the initial concentrations of Pb (II) ions at optimum pH values and 90 min of equilibration time. As shown in Fig. 5, the adsorbed amount of metal ions by the ionic SCS adsorbent was dependent on the initial metal ion concentration in the solution. When the initial Pb(II) ion concentration was increased from 20 mg/L up to 100 mg/L, the adsorption capacity of SCS1, SCS2, and SCS3 increased from 1.502 to 4.421 mg/g, 1.911 to 5.812 mg/g, and 2.114 to 6.910 mg/g, respectively. The SCS3 adsorption capacity was much better than others. The increasing adsorption capacity of SCS might be attributed to the fact that the increasing initial concentration could increase the contact of surface solid-liquid, resulting in

the higher collision between Pb (II) ions and the SCS sorbent material. Moreover, the adsorption trends among three samples were similar, which implied that the types of adsorption isotherms of them were alike.

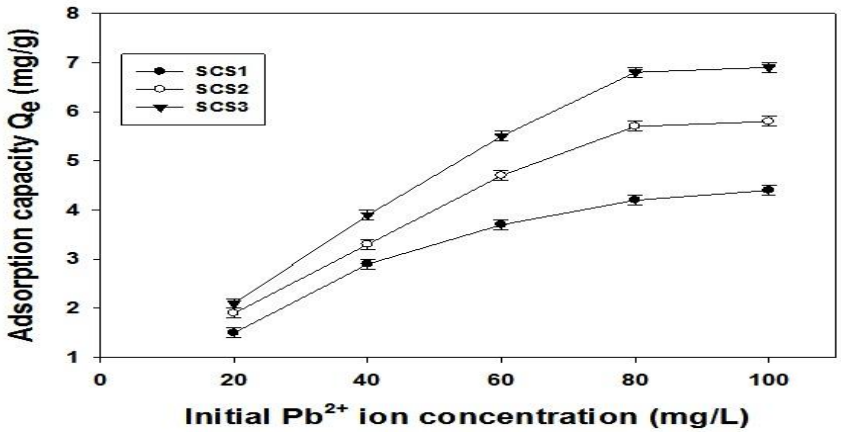


Fig.5. Effect of initial concentration of Pb (II) on SCS adsorbent.

3.3.3. Adsorption isotherm

Equilibrium data, commonly known as adsorption isotherm, are basic requirements for designing of adsorption systems [12]. In this work, the equilibrium data for Pb^{2+} onto SCS adsorbent was evaluated with Langmuir model. A good linearized plot of Ce/Qe versus Ce could be seen in Fig. 6, which gave the values of K_a and Q_m in Table 2 according to the intercept and slope of these lines, respectively. The correlation coefficients of SCS1, SCS2 and SCS3 are R^2= 0.9992, 0.9997 and 0.9999, respectively. It is noteworthy that monolayer capacity (Qm) of the SCS adsorbent for the Lead is comparable to the maximum adsorption obtained from the adsorption isotherms.

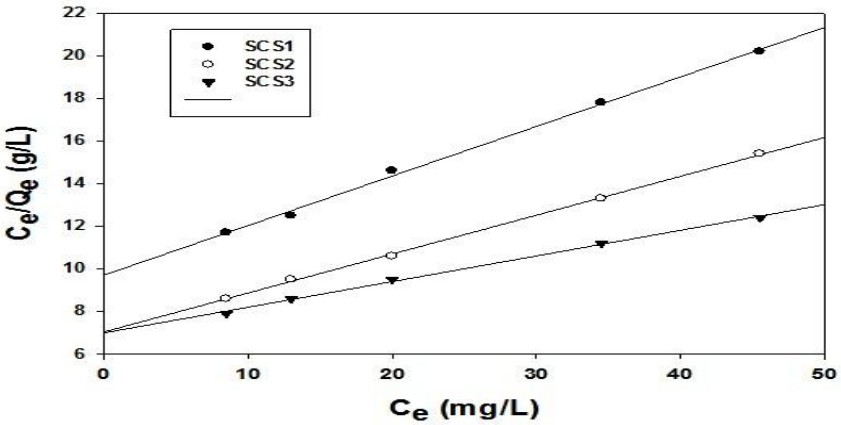


Fig.6. Langmuir adsorption isotherm for the adsorption of Pb (II) ion on SCS adsorbent.

Table 2

Langmuir parameters for three kinds of SCS

Sample	Q_m (mg/g)	K_a (mg/L)	R^2
SCS1	4.411	0.0206	0.9992
SCS2	5.814	0.0228	0.9997
SCS3	6.922	0.0258	0.9999

3.4. Desorption and Repeated use

To make the any sorbent economically competitive, ions adsorbed must be released from the sorbent in order to reuse the material. The results in Fig.7 showed the quantity of Pb (II) ions adsorbed on SCS from four repeated adsorption-desorption cycles. It was found that the SCS sorbent could be used repeatedly without losing their adsorption capacities significantly, with high desorption percentages (97%).

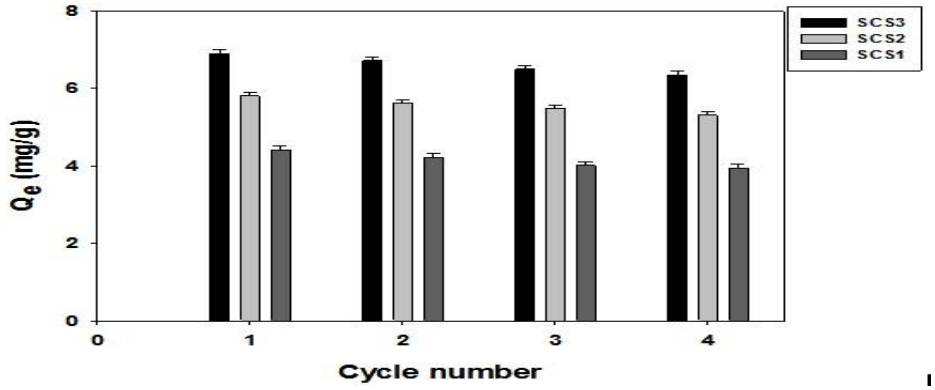


Fig.7. Binding amount of the SCS for Pb (II) ions in four adsorption-desorption cycles.

IV. Concluding Remarks

Corn starch succinylated with succinic anhydride in an aqueous alkaline medium has been shown to be a rather capable sorbent for adsorbing Pb (II) ions from aqueous samples. The adsorption between Pb (II) ion and the succinylated starches (SCSs) was found to be dependent on the pH of the solution, as well as the initial concentration of Pb^{2+} ion. Maximum removal of lead on SCS was at pH 6.0. The SCS adsorbent was suitable for repeated use without considerable loss of adsorption capacity. As effective and biodegradable adsorbent, SCS may have great potential application for the removal of Pb (II) ions from waste water. Work to verify that immobilization of 2, amino-4,6-dihydroxylpyrimidine ligand on the surface of the starch molecules could be used for the adsorption of Cu (II) ions is currently underway.

V. Acknowledgements

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