Isotherms, kinetics and equilibrium Studies of adsorption of Lead (II) ions from aqueous solutions Using Polymer-Modified Coconut Shell Activated Carbon (MCSAC)

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Abstract: Coconut (Cocos nucicera L) shell activated carbon was modified with urea immobilized-polysiloxane, and its potential for the removal of Pb2+ from simulated water samples was studied. It was activated physically to generate the modified coconut shell activated carbon (MCSAC). The functional groups and image morphology of the activated carbons were analyzed using Fourier transform infrared (FTIR) spectroscopy and Scanning Electron Microscope (SEM) respectively. Batch adsorption experiment were carried out using available MCSAC adsorbent for the removal of Pb(II) ions from aqueous solutions. The effect of the initial Pb2+ concentration, contact time, adsorbent dosage, temperature and pH were experimentally studied in batch mode to evaluate the adsorption capacity, kinetic and equilibrium. Experimental results revealed that optimal adsorption took place at pH 8.0 and high lead (II) concentration 200 mg/l. The uptake process obeyed the pseudo-second-order kinetic expression and was best described by Harkins-Jura isotherm than other models (Langmuir, Freundlich and Temkin) considered. Thus, MCSAC could be employed as low-cost alternative for removal of Pb2+ from industrial wastewater.

Keywords: Adsorption isotherm, kinetics, lead (II) ions, activated carbon from coconut shell, modification with polymer

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I. Introduction
In recent years, Heavy metals are considered trace elements because of their presence in trace concentration. They are metallic elements with relatively high density, toxic or poisonous 1, they are naturally occurring non-biodegradable elements that are found in the earth’s crust. Their existence has been a menace to the environment and have drawn global concern. Their occurrence and depositions from various manufacturing processes has created a serious environmental issue in the sense that, excessive concentrations of these metals are detrimental and destabilizes the ecosystems through bioaccumulation in organisms, body, and food chain, causing toxic effects on living organisms by metabolic interference and mutagenesis 2. Toxicity and persistence in the environment are the major risk exhibits by most of these metals and these has also become a major threat to plant, animals and human life, therefore, must be removed from municipal and industrial effluents. Excessive exposure and intake of these metals, including arsenic, nickel, lead, and cadmium, has been associated with various diseases, such as cancer, cardiovascular and neurological diseases 3. Humans also suffers accumulative poisoning, nervous system damage, lowering of the reproductive activities of organisms, inhibition of growth, as well as death in most living beings.

Apart from the earth’s crust, heavy metals are released into the environment by both natural and anthropogenic activities such as milling, mining, smelting operations, industrial activities, domestic and agricultural use of metals and metal compounds. Other sources of heavy metal contamination into the environment are through metal corrosion, atmospheric deposition, soil erosion of metal ions and leaching of heavy metals 4.

Lead is one of the heavy metals considered toxic to humans, animals, fishes and environment. Some of the major sources of lead released into the environment are from metal finishing industries, paint manufacture, electroplating, metallurgical industry, petroleum refining, fuel combustion, photographic materials, lead-acid battery manufacture and drainage from ore and mines 5. Drinking water delivered through lead pipes or pipes joined with lead solder may contain lead 5.
Water contamination or pollution with heavy metals are the major problem mitigating against the environment, which are caused by the influence of the heavy metal depositions on soil, water and air. It is suffered mostly in the developing and underdeveloped countries. Many methods have been developed for the treatment and removal of heavy metals concentrations. These methods are expensive, time consuming, differ in their efficiency and can generate toxic sludge and some requires higher energy. Some of the methods are chemical precipitation, filtration, ion exchange, reverse osmosis, sedimentation, solvent extraction, ultrafiltration, electrochemical deposition, coagulation and adsorption. However, the above mentioned conventional methods are not economically viable for small and medium size industries due to huge capital requirements. It is therefore necessary to search for low cost alternative techniques that may be effective, economical and sludge free.

According to report by Uddin, that for trace metal ions concentration in wastewater, the adsorption process is suitable for their removal because they are highly efficient, effective, cheap, simple, sludge free, ease of operation, insensitive to toxic substances, less environmentally degrading and easy recovery. In this case, activated carbon is preferred and seems to be more viable option for removal of lead from wastewater. Activated carbon is an amorphous form of elemental carbon prepared from variety of carbonaceous raw materials, including wood, coal or coconut shells. It is unique and effective agent for purification, isolation and recovery of trace materials. With better awareness of the problems associated with lead came increase in research studies related to treatment methods. Many adsorbent from agricultural by-products have been applied for the removal of lead (II) ions such as activated carbon from the precursors; plantain peels, palm kernel shell, eggshells, thevetia neriifolia nutshell, rice husk, Date pit, Nano-silver coated activated carbon, Cedar leaf, coconut husk, coconut shell.

Coconut shell is an attractive and economic alternative for the removal of metal ions from waste water. In this work, coconut shell adsorbent was modified with immobilized polysiloxanes, to increase the functional group and improve selective properties of coconut shell to adsorb the heavy metal Pb (II) through the formation of coordination compound between them. The characterization of the modified coconut shell was carried out by analyzing the fourier Transform Infrared Spectrum (FT-IR) and Scanning Electron Microscopy (SEM) of the adsorbent. The aim of this work was to study the adsorption capacity of coconut shell that was modified with inorganic polymer (polysiloxane) for the removal of Pb (II) ions from aqueous solutions. The effects of initial metal ion concentration, contact time, temperature, pH and adsorbent dosage on the adsorption efficiency were also investigated. In addition, the equilibrium data was tested on adsorption isotherms; Freundlich, Langmuir, temkin and Harkins-Jura models. And kinetic models are applied on experimental data to observe the kinetic behavior of adsorption process.

II. Material And Methods

2.1 Materials and Instruments

All the reagents used in this work was of analytiacal grade; lead nitrate, Pb(NO₃)₂, (99 % Labosi, India), NaOH, and HCl. The instruments used was Flame Atomic Absorption Spectrophotometer FS240AA Agilent U.S.A., Buck scientific M530 USA FTIR was used for the analysis, and SEM-Phenom ProX by Phenom World Eindhoven, netherlands.

2.2 Methods

2.2.1 Preparation of Coconut shell activated carbon (CSAC)

The activation process was physical method. Coconut shell was gathered from urban area of Ogbete main market Enugu State. They were thoroughly washed with sponge and clean water severally to remove dirt and after with distilled water. They were air-dried for 3 days before being finally oven-dried at 105°C for 5 hr. The dried shells was weighed and it was 2.3 kg. Then crushed into smaller pieces for easy activation. And was loaded into a heat chamber of electric heat muffle furnace to pyrolyse in the absence of air, at temperature raised to 650°C for 1.30 min, then the furnace was switch off. The substance was kept to cool overnight, after that, the activated carbon was collected, grounded and sieved to fine particles. The weight was 1.15 kg and then stored in air tight container for further use.

\[
\text{% Yield} = \frac{\text{Weight of the final product}}{\text{Weight of the initial sample}} \times 100
\]

2.2.2 Preparation of urea immobilized polysiloxane

Tetraethoxysilane (20.83g) was mixed with 15 cm³ of methanol and 9.95 cm³ of HCl (0.42 g/cm³) and stirred very well. 3-chloropropyltriethoxsilane was then added to the mixture and stirred. Gelation occurred after few seconds, and the product was allowed to stand for 12 h, at ambient temperature (room temperature) and then dried in an oven at 90°C. The dried product was grounded, sieved, and washed successively with 50 cm³ portions of 0.025 g/cm³ NaOH, water, methanol and diethylether. It was dried again in an oven at 90°C for 10 h.
The product (1.0g) was refluxed with 0.98 g of urea in 50 cm³ of toluene at 110°C for 10 h. After which, it was allowed to cool, filtered, and washed with equal portion of 50 cm³ water, methanol, and diethyl ether, and dried at 90°C and 1 atm. for 10 h.

2.2.3 Modification of activated carbon (CSAC) with urea immobilized polysiloxane

0.5g of the prepared urea immobilized polysiloxane was added to small quantity of de-ionized water. 20g of the activated carbon was added and mixed properly. The mixture was dried in an oven at 50°C at 150 rpm for about 45 min. After which, the modified coconut shell activated carbon (MCSAC) formed was ready to be used for the adsorption experiments.

2.3 Characterization of the Unmodified and Modified coconut shell activated carbon (MCSAC).

2.3.1 FT-IR Analysis: The CSAC and MCSAC samples were analysed to detect the functional groups present in them using Fourier transform infrared spectroscopy (FTIR). The region of infrared was between 4000 and 600 cm⁻¹ at room temperature.

2.3.2 SEM Analysis: The morphology of the CSAC and MCSAC samples were analyzed using the scanning electron microscope (SEM), operated at 15 kV, to determine the changes in the surface microstructures of the activated carbons.

2.4 Preparation of 1000 ppm Pb(NO₃)₂ (simulated water) solution

Synthetic wastewater samples were prepared by using analytical grade lead nitrate, Pb(NO₃)₂ (99 % Labosi, India) in double distilled water. To prepare 1000 ppm of Pb(NO₃)₂, 1.599g of Pb(NO₃)₂ was weighed and then dissolved in 100 cm³ of water and made up to the mark of 1000cm³ standard volumetric flask to give 1000 ppm Pb(NO₃)₂ stock solution. Then Working solutions of 50, 100, 150, and 200 mg/L were prepared from the stock by dilution.

2.5 Batch adsorption experiments

The batch experiments were performed by adding 10 cm³ each of the various concentration (50, 100, 150 and 200 mg/l) of the stock solution in a set of test tubes containing initial adsorbent dose (1g), pH 6.5, and at temperature 20 °C. The solution was shaken using a mechanical Gemmy orbit shaker (model: VRN-480, USA) at 100 rpm for 20 minutes to establish equilibrium condition. After equilibrating, the content of each tube was filtered using a whiteman filter paper and the free ion concentration of lead(II) in the filtrate was determined using HANNA instruments pH meter (pH 209 model, Portugal). All experiments were performed at volume (10 cm³), and 100 rpm. The pH of the original solution and the filtrate solution was determined using HANNA instruments pH meter (pH 209 model, Portugal).

The amount of lead ions adsorbed qₑ in mg/l can be expressed as

\[ qₑ = \frac{Cₒ - Cₑ}{W} \times V \]  

Here, The amount of lead ion adsorbed per unit mass of the adsorbent (amount adsorbed in mg/g), qₑ and (%) removal was evaluated using the following equations:

\[ qₑ = \frac{(Cₒ - Cₑ)}{W} \times 100 \]  

Where; Cₒ is the initial ion concentration in mg/l, Cₑ is the metal ion concentration at equilibrium in mg/l, V is the volume of metal ion solution in litres, and W is the amount of adsorbent used in gram.

2.6 Adsorption isotherms

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the homogeneity or heterogeneity of adsorbents. The nature of adsorption was evaluated by fitting the data obtained into Langmuir, Freundlich, Temkin, and Harkins-Jura isotherms, in order to find the best model that represents the equilibrium data for Pb²⁺ adsorption onto MCSAC adsorbent.

2.6.1 Langmuir isotherm: defines a monolayer adsorption on a homogenous surface even at higher adsorbate concentrations. This assumption is expressed mathematical by non linear relation given as:

\[ qₑ = \frac{qₘ K L Cₑ}{1 + K L Cₑ} \]  

Where, qₑ is the amount of Pb(II) ions adsorbed on the MCSAC adsorbent at equilibrium (mg/g), Cₑ is the equilibrium concentration of the Pb(II) ions in the solution (mg/l), qₘ and KL are the Langmuir constants.

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\[ q_m = \text{the maximum monolayer adsorption capacity of the adsorbent (mg/g)} \]
\[ K_e = \text{the energy constant related to the heat of adsorption (related to affinity of binding sites).} \]

Equation (4) can be re-arranged in the linear form as:

\[ \frac{1}{q_e} = \frac{1}{q_m K_e} + \frac{1}{q_m} \]  
(5)

\[ q_m \text{ and } K_e \text{ was obtained by plotting } 1/q_e \text{ versus } C_e \text{ from equation (5). The slope and intercept of the straight line graph gotten gave the values of these constants } q_m \text{ and } K_e \text{ as shown in table ....} \]

2.6.2 Freundlich isotherm: defines a multilayer adsorption on a heterogeneous surface of suitable energies. It assumes that heterogenous or different sites with several adsorption energies are involved (non-uniform distribution of sorption heat) \(^{33}\). The non linear equation is represented by:

\[ q_e = K_f C_e^{1/n} \]  
(6)

The Freundlich isotherm is represented by the Linear Logarithm equation:

\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]  
(7)

where, \( q_e \) is the amount of the adsorbate (Pb\(^{2+}\)) adsorbed on the MCSAC adsorbent at equilibrium (mg/g); \( C_e \) is the equilibrium concentration of the Pb (II) ions in the solution (mg/l); \( K_f \) and \( 1/n \), are the Freundlich constants. \( K_f \) is an indicator of adsorption capacity.

2.6.3 Temkin isotherm: Temkin isotherm is used for heterogeneous surface energy system. The linear form is expressed as:

\[ q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \]  
(8)

\[ q_e = B \ln K_T + B \ln C_e \]  
(9)

Where, \( B \) and \( K_T \) are temkin constants, \( B = \frac{RT}{b} \) which related to heat of sorption (J/mol), \( R \) is gas constant (8.314 J\(^{\text{mol}}\)K\(^{-1}\)), \( T \) is temperature in Kelvin (k) and \( K_T \) is the adsorption potential or the equilibrium binding constant (L/g or L/mol) corresponding to the maximum binding energy and interaction between adsorbate and adsorbent \(^{30}\). The adsorption data can be analyzed with equation (9). A plot of \( q_e \) versus \( \ln C_e \) gives the value of constants \( B \) and \( K_T \) as listed in Table 13.0

2.6.4 Harkins-Jura isotherm: This isotherm accounts for multilayer adsorption and can be explained with the existence of a heterogeneous pore distribution \(^{31}\). Harkins Jura adsorption isotherm can be expressed as:

\[ \frac{1}{q_e} = \frac{1}{A_{HJ}} - \frac{1}{A_{HJ}} \log_{10} C_e \]  
(10)

Where, \( A_{HJ} \) is Harkins-Jura isotherm parameter which accounts for multilayer adsorption and explains the existence of heterogeneous pore distribution, \( B_{HJ} \) is the isotherm constants.

2.7 Adsorption kinetics

Kinetic models are time dependent models that can be used to examine the rate of adsorption process and the potential rate-controlling step on the adsorbent surface \(^{32}\). To examine the adsorption kinetics of lead (II) ions, the pseudo-first-order and pseudo-second-order were applied to the experimental data.

2.7.1 Pseudo-first-order: The pseudo first order rate equation is one of the most widely used equations for the adsorption of a solute from an aqueous solution and can be expressed in the linear form \(^{33}\):

\[ \log (q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \]  
(11)

Where, \( q_e \) and \( q_t \) are the amount of metal ion adsorbed (mg/g) at equilibrium and time, \( t \), respectively. \( K_1 \) is the first-order reaction rate constant (min\(^{-1}\)). A plot of \( \log(q_e - q_t) \) versus \( t \), gives a linear relationship, from which the value of \( K_1 \) and \( q_e \) can be determined from the slope and intercept \(^{34}\).

2.7.2 Pseudo-second-order: The linear form of the pseudo second order kinetic rate is given as \(^{35}\):

\[ \frac{t}{q_t} = \frac{t}{k_2 q_e^2} + \frac{1}{q_e} \]  
(12)

Where, \( q_e \) is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g), \( q_t \) is the amount of adsorbate adsorbed at contact time \( t \) (mg/g) and \( K_2 \) is the pseudo-second-order rate constant (gmg\(^{-1}\)min\(^{-1}\)). A plot of \( t/q_t \) versus \( t \) gives a linear relationship, from which \( q_e \) and \( K_2 \) can be determined from the slope and intercept \(^{36}\).

2.8 Statistical analysis(10 Bold)
Data was analyzed using Microsoft Excel 2007.

III. Results and Discussion

3.1 characterization of activated carbon
In this study, both coconut shell activated carbon (CSAC) and modified coconut shell activated carbon were characterized.
3.1.1 Adsorbent properties
Surface area, bulk and particle density were directly related to the development of porosity of activated carbons. The increase in the ratio of polymer/sample promotes an improvement of the surface area (from 650 m²/g to 768 m²/g) and porosity (from 0.635 to 0.688). Porosity varies depending on particle size and aggregation. Porosity decreases as bulk density and particle density increases or vice versa as seen in Table 1.0.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Bulk density (g/cm³)</th>
<th>Particle density (g/cm³)</th>
<th>Surface area (m²/g)</th>
<th>Porosity (%)</th>
<th>Ash content (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSAC</td>
<td>0.847</td>
<td>1.333</td>
<td>650</td>
<td>0.635</td>
<td>1.475</td>
<td>50</td>
</tr>
<tr>
<td>MCSAC</td>
<td>0.762</td>
<td>2.442</td>
<td>768</td>
<td>0.688</td>
<td>2.092</td>
<td></td>
</tr>
</tbody>
</table>

3.1.2 Structural morphology
The surface morphology of the activated carbon before and after modification with polymer was evaluated using Scanning electron micrographs (SEM) as shown in figure 1.0a, b. The micrograph showed clearly different surfaces. Fig.1.0a shows that the surface of unmodified activated carbon (CSAC) was rough, irregular and closed with impurities that might be seen from Energy dispersive X-ray (EDX) elemental micro-analysis in fig. 2.0c,d, and might have contributed to its low porous properties. However, Fig. 1.0b show that modified activated carbon (MCSAC) has improved surface morphology with better porous surface as a result of removal of impurities attached on the surface as seen in EDX elemental table below, which proved that some percentage of metals disappeared from the surface given 95.75 percent atomic concentration of carbon while some such as Tantalum and sodium appeared after modification.

![Fig.1.0 SEM image of (a) unmodified CSAC and (b) modified CSAC](image)

![Fig. 2.0c: EDX spectra pattern elemental analysis for unmodified -CSAC](image)
### 3.1.3 FTIR measurements

Fourier transform infrared (FTIR) spectroscopy was used to evaluate the functional groups on the surface of CSAC and MCSAC at frequency regions of 4000 – 600 cm\(^{-1}\) as shown in Figure 3.0(e) &f, and co-added at 32 scans and at 4 cm\(^{-1}\) resolution. FTIR spectra were displayed as transmitter values, and several peaks assigned to the vibrations of the CSAC and MCSAC functional groups were detected. Some other ones appeared or added as a result of modification, while some due to wavelength shift in the process. The measurement showed the presence of some functional groups in Table 2.0.

![Fig. 2.0d: EDX spectra pattern elemental analysis of modified-CSAC](image)

<table>
<thead>
<tr>
<th>Adsorption band (cm(^{-1}))</th>
<th>Appearance</th>
<th>Type of vibration</th>
<th>Type of bond</th>
<th>Functional groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSAC</td>
<td>MCSAC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3828.552 - 3592.012</td>
<td>3879.178 - 3632.936</td>
<td>medium, sharp</td>
<td>stretching</td>
<td>O-H &quot;free&quot; Hydroxyl of carboxylic, alcohols and phenols</td>
</tr>
<tr>
<td>3457.103 - 3269.187</td>
<td>3521.839 - 3231.759</td>
<td>strong, broad</td>
<td>stretching</td>
<td>O-H &quot;intermolecular bonded&quot; Hydroxyl groups</td>
</tr>
<tr>
<td>3019.095 - 288.186</td>
<td>3031.678 - 2970.288</td>
<td>Medium</td>
<td>stretching</td>
<td>C-H assymetric of methyl, methylene and methoxy groups</td>
</tr>
<tr>
<td>2751.351</td>
<td>2784.491</td>
<td>Medium</td>
<td>stretching</td>
<td>O=CH aldehyde with structure -CHO</td>
</tr>
<tr>
<td>2601.215</td>
<td>2669.237 - 2522.666</td>
<td>Weak</td>
<td>stretching</td>
<td>S-H weak stretching thiol</td>
</tr>
<tr>
<td>2145.998</td>
<td>2178.303 - 2089.274</td>
<td>Strong</td>
<td>stretching</td>
<td>C=N cyanates of nitrile groups</td>
</tr>
<tr>
<td>1974.948</td>
<td>1981.481</td>
<td>Medium</td>
<td>stretching</td>
<td>C=C=C allene</td>
</tr>
<tr>
<td>1857.628</td>
<td>1869.205 - 1702.776</td>
<td>Strong</td>
<td>stretching</td>
<td>C=O ketones, aldehydes, ester, carboxylic groups</td>
</tr>
<tr>
<td>1630.752</td>
<td>1609.396</td>
<td>Medium</td>
<td>stretching</td>
<td>C=C alkene, aromatic ring</td>
</tr>
<tr>
<td>1374.225</td>
<td>1388.12 - 1312.86</td>
<td>Strong</td>
<td>stretching</td>
<td>S=O sulfonyl chloride, sulphonates</td>
</tr>
<tr>
<td>1277.913 - 1106.068</td>
<td>1133.473 - 931.543</td>
<td>Strong</td>
<td>stretching</td>
<td>C=O-C, C-O Stretching vibrations of carbohydrates</td>
</tr>
<tr>
<td>841.1585 - 767.8679</td>
<td>727.0389</td>
<td>Strong</td>
<td>bending</td>
<td>C-H, C-Cl aromatics bonds alkenes and halogeno compound</td>
</tr>
</tbody>
</table>

Table 2.0: FTIR adsorption bands, functional groups and interpretation for CSAC and MCSAC
3.2 Effect of concentration:

The effect of initial ion concentration on the adsorption efficiency of the MCSAC was studied. Adsorption experiments were carried out at different initial ion concentrations ranging from 50 to 200 mg/l. The percentage of Pb\(^{2+}\) removed at 50, 100, 150 and 200 mg/l levels are 62.83, 38.02, 80.63 and 99.07% respectively as seen in Table 3.0. The optimal concentration where high percentage removal were observed was 200 mg/l. It was also observed as a trend that there is an increase of the percentage removal with increase in initial concentration of Pb\(^{2+}\) ion. These may be as a result of adequate active sites in the adsorbent even at higher concentrations.\(^{39}\) Thus, more Pb\(^{2+}\) ions were adsorbed from solution at higher concentration level. It is therefore evident that at low concentration, the active sites on the adsorbent surface are not completely covered, so more ions would probably get adsorbed on increase of the initial concentration.\(^{40}\) Also, from the graph of quantity adsorbed (\(q_e\)), between 100 mg/l and 150 mg/l, there is a bit curve seem slow down, it’s not a sign of decrease but a sign of sharp increase at higher range of concentration margin which brings about an even increment in the amount adsorbed. The optimal percentage removal and amount adsorbed are 98.78 % and 335.08 mg/g respectively.

<table>
<thead>
<tr>
<th>Initial Concentration (mg/l)</th>
<th>(C_e)</th>
<th>% Removal</th>
<th>(q_e) (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.242</td>
<td>62.83</td>
<td>4.09</td>
</tr>
<tr>
<td>100</td>
<td>0.326</td>
<td>65.97</td>
<td>6.32</td>
</tr>
<tr>
<td>150</td>
<td>0.352</td>
<td>80.63</td>
<td>14.65</td>
</tr>
<tr>
<td>200</td>
<td>0.414</td>
<td>98.78</td>
<td>335.08</td>
</tr>
</tbody>
</table>

Table 3.0: % Removal of the Pb\(^{2+}\) at various concentrations, pH 6.5, 100 rpm, 20 min. at 20 °C using 1.0g of MCSAC adsorbent.
3.3 Effect of contact time

The effect of contact time on the adsorption of Pb$^{2+}$ was studied at different agitation times 5, 10, 15 and 20 min. for Lead concentration of 200 mg/l at room temperature 20 $^\circ$C, pH 6.5 and 100 rpm. Adsorption as a function of time was evaluated in order to determine the equilibrium time required for maximum adsorption of Pb$^{2+}$. Figure 5.0 show the adsorption of the lead ions using MCSAC. It also showed that the rate of adsorbed Pb$^{2+}$ onto MCSAC was initially rapid and increases as time progresses until it reaches the optimum where the surface coverage of the adsorbent is high at 15 min. and then it slowed down. It is observed that the concentration of lead ions adsorbed on the MCSAC increased with increase in agitation time. This could be due to the migration of higher fraction of Pb$^{2+}$ from the bulk solution through the adsorbent boundary layer onto the active sites of the adsorbent as time progresses $^{22}$, or due to the decrease in boundary layer resistance to mass transfer in bulk solution and also increase in kinetic energy of the hydrated Pb$^{2+}$ $^{22}$.

Table 4.0: % Removal of the Pb$^{2+}$ at various Contact Time at 20 $^\circ$C using 200mg/l on 1.0 g of MCSAC adsorbent at 100rpm

<table>
<thead>
<tr>
<th>Contact Time (min)</th>
<th>Ce</th>
<th>% Removal</th>
<th>$q_e$ (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.41</td>
<td>98.79</td>
<td>335.12</td>
</tr>
<tr>
<td>10</td>
<td>0.40</td>
<td>98.82</td>
<td>335.22</td>
</tr>
<tr>
<td>15</td>
<td>0.25</td>
<td>99.26</td>
<td>336.72</td>
</tr>
<tr>
<td>20</td>
<td>0.30</td>
<td>99.12</td>
<td>336.22</td>
</tr>
</tbody>
</table>

3.4 Effect of Adsorbent dose

The effect of adsorbent dosage on the adsorption of Pb$^{2+}$ was studied at various dosages 0.2, 0.4, 0.6 and 0.8 g, keeping other parameters (concentration, time, pH, and temperature) at constant value. From the data obtained, it was observed that with increasing amount of adsorbent, the percentage removal first increases to 99.71% , reaches maximum at 0.2 g and then decreases. Also, Pb(II) uptake (quantity adsorbed or adsorption capacity) $q_e$ decreases as adsorbent dosage increases as shown in Figure 6.0. According to report by Padmavathy $^{41}$, at lower adsorbent, concentration number of active sites is still higher, but with the increase in adsorbent dosage, aggregation of particles take place. As a result of that, the efficiency and Pb$^{2+}$ uptake decreases.
Table 5.0 shows the variation of % removal of ions adsorbed with different grams of adsorbent. From the graph, it was clearly observed that the percentage removal and adsorption capacity \( q_e \) decreased sharply with the increasing of adsorbent dosage. Moreover, the high adsorbent dosage could impose a screening effect of the dense outer layer of the cells, thereby shielding the binding sites from metal.

**Table 5.0:** % Removal of the Pb\(^{2+}\) at various Adsorbent Dose at 20 \(^\circ\)C, using 200mg/l at 100 rpm for 15 min of MCSAC adsorbent

<table>
<thead>
<tr>
<th>Adsorbent Dose (g)</th>
<th>Ce</th>
<th>% Removal</th>
<th>Quantity Adsorbed ( q_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.10</td>
<td>99.71</td>
<td>1691.10</td>
</tr>
<tr>
<td>0.4</td>
<td>0.39</td>
<td>98.85</td>
<td>845.05</td>
</tr>
<tr>
<td>0.6</td>
<td>0.13</td>
<td>99.62</td>
<td>563.20</td>
</tr>
<tr>
<td>0.8</td>
<td>0.16</td>
<td>99.53</td>
<td>422.03</td>
</tr>
</tbody>
</table>

**Figure 6.0:** Effect of Adsorbent Dose (%Removal and Quantity adsorbed, \( q_e \))

### 3.5 Effect of temperature

The effect of temperature on the lead adsorption on the adsorbent (MCSAC) was investigated at different temperatures 20°C, 40°C, 60°C and 80°C. The maximum adsorption value for Pb\(^{2+}\) solution was 99.51% at 20 °C as shown in Figure 7.0, it may be due to the initial availability of the active sites, pore size and activation of the adsorbent surface. Also, the adsorption capacity of Pb\(^{2+}\) onto MCSAC as seen in figure 7.0 was initially high and decreases as temperature increases until it reaches where the surface coverage of the adsorbent is high at 80°C. In some cases, increase in temperature results in swelling of lignocellulosic material of an adsorbent, thus enabling the large lead molecule to penetrate further which in turn adsorbed in the inner binding sites, and may result to an endothermic process.

**Table 6.0:** % Removal of the Pb\(^{2+}\) at various Temperature using 200mg/l at 100 rpm for 15 min of 0.2 g MCSAC adsorbent

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Ce</th>
<th>% Removal</th>
<th>( q_e ) (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.167</td>
<td>99.51</td>
<td>1687.75</td>
</tr>
<tr>
<td>40</td>
<td>0.211</td>
<td>99.38</td>
<td>1685.55</td>
</tr>
<tr>
<td>60</td>
<td>0.632</td>
<td>98.14</td>
<td>1664.50</td>
</tr>
<tr>
<td>80</td>
<td>0.800</td>
<td>97.64</td>
<td>1656.10</td>
</tr>
</tbody>
</table>
3.6 Effect of pH

pH is one of the most important factors in controlling the adsorption process. It affects the solubility of the Pb (II) ions concentration of the counter ions on the functional group of the adsorbent and the degree of ionization of the adsorbate during reaction. Thus, the effect of the initial pH value on the uptake capacity of MCSAC towards Pb (II) ions was investigated over the pH range 2, 4, 6 and 8, employing the optimal values obtained in the previous experiments which includes 10 ml of the initial Pb (II) ion concentration of 200 mg/l, 0.2 g of adsorbent, 20°C, at 100 rpm for 15 min. At initial pH of 2.0, the percentage of Pb^{2+} ions removed was a bit high but decreases with increasing pH, and reached maximum at 95.65%. The variation of the equilibrium uptake of Pb(II) ions with the initial pH value is depicted in Table 7.0, which indicates that the maximum adsorption capacity of MCSAC towards Pb (II) ions (q_e), was 1622.30 mg/g at pH value of 8.0. Which shows that alkaline medium tend to support adsorption more than acidic medium. At low pH values, the surface of the absorbent would be closely associated with hydroxonium ions, by repulsive forces, to the surface functional groups, consequently decreasing the percentage adsorption of metal. At lower pH value, the H^{+} ions compete with the metal cations for the adsorption sites in the system. As the pH increases, the onset of the metal hydrolysis and precipitation begins following the resultant adsorption which occurs before the beginning of hydrolysis.

Table 7.0: % Removal of the Pb^{2+} ions at various pH values using 200mg/l at 20 °C, 100 rpm for 15 min of 0.2g MCSAC adsorbent

<table>
<thead>
<tr>
<th>PH</th>
<th>Ce</th>
<th>% Removal</th>
<th>q_e (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>6.242</td>
<td>81.60</td>
<td>1384.00</td>
</tr>
<tr>
<td>4</td>
<td>8.707</td>
<td>74.33</td>
<td>1260.75</td>
</tr>
<tr>
<td>6</td>
<td>12.056</td>
<td>64.46</td>
<td>1093.30</td>
</tr>
<tr>
<td>8</td>
<td>1.476</td>
<td>95.65</td>
<td>1622.30</td>
</tr>
</tbody>
</table>

Figure 8.0: Effect of pH (% Removal and Quantity adsorbed, q_e)
3.7 Adsorption isotherms
3.7.1 Langmuir isotherm

Despite the high correlation coefficients ($R^2 = 0.914$) in Langmuir model compared to that of Freundlich ($R^2 = 0.700$) and Temkin ($R = 0.504$), the negative slope and the negative which reflected in Langmuir isotherm constants ($q_m, K_L$ and $R_L$) resulting from the model calculations indicate that this model is inadequate to explain this adsorption process $^{44, 45, 46}$. Also, the essential characteristics of this Langmuir isotherm model can be expressed in terms of a dimensionless separation factor for equilibrium parameter, $R_L$ $^{47}$, which is defined as:

$$R_L = \frac{1}{1 + K_L C_o} \quad (13)$$

Where, $K_L$ is the Langmuir constant which indicates the nature of adsorption (L/mg), $C_o$ is the initial Pb(II) concentration (mg/l). The separation factor $R_L$ indicates the isotherm shape and whether the adsorption is favourable or not, based on the given criteria: Linear ($R_L = 1$), Unfavourable ($R_L > 1$), Favourable ($0 < R_L < 1$), Irreversible ($R_L = 0$) and unfavourable adsorption $R_L < 1$ $^{44, 48}$.

In this work, we evaluated the separation factor $R_L$ for all concentrations to determine whether the adsorption is favourable for the whole range. From Table 8.0, the $R_L$ were found to be -2.0928 to -0.0132 for the initial concentrations of 50 to 200 mg/l Pb (II), and the maximum monolayer coverage capacity ($q_m$) for Pb (II) ions from Langmuir isotherm model was determined to be -3.2154 mg/g. Langmuir isotherm constant ($K_L$) and the separation factor ($R_L$) exhibiting negative values as shown in Table 8.0 and 12.0, indicates that the equilibrium sorption was not favourable, that is $R_L < 0$, and there is a tendency of desorption in the progression.

Table 8.0: Equilibrium experimental data for Langmuir investigation of Pb (II) ions per unit gram of MCSAC adsorbents.

<table>
<thead>
<tr>
<th>Initial Concns (mg/l)</th>
<th>Ce</th>
<th>$q_e$ (mg/g)</th>
<th>$R_L$</th>
<th>$1/q_e$</th>
<th>$1/Ce$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.242</td>
<td>4.09</td>
<td>-2.0928</td>
<td>0.2445</td>
<td>4.13223</td>
</tr>
<tr>
<td>100</td>
<td>0.326</td>
<td>6.32</td>
<td>-0.8512</td>
<td>0.1582</td>
<td>3.06748</td>
</tr>
<tr>
<td>150</td>
<td>0.352</td>
<td>14.65</td>
<td>-0.3200</td>
<td>0.0683</td>
<td>2.84091</td>
</tr>
<tr>
<td>200</td>
<td>0.414</td>
<td>335.08</td>
<td>-0.0132</td>
<td>0.0030</td>
<td>2.41546</td>
</tr>
</tbody>
</table>

Figure 9.0: Langmuir isotherm plot for adsorption of Pb (II) onto MCSAC

3.7.2 Freundlich isotherm

The ability of Freundlich model to fit the experimental data was examined. Thus, the plot of $\ln q_e$ versus $\ln C_e$ was employed to generate the intercept value of $\log K_f$ and the slope of $1/n$. $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero $^{47}$. $n$ is an empirical parameter which reflects the effect of concentration on the adsorption capacity and represents the intensity of adsorption that varies with the degree of heterogeneity. The adsorption process is
Isotherms, Kinetics And Equilibrium Studies Of Adsorption Of Lead (II) Ions From Aqueous ...

said to be favourable when the value of $n$ satisfies the condition $1 < n < 10$, otherwise it is unfavourable $^{35,46}$. As we can see in Table 12.0, the value of $n$ is outside the range of 1–10 indicating unfavourable adsorption process.

**Table 9.0**: Equilibrium experimental datas for Freundlich investigation of Pb (II) ions per unit gram of MCSAC adsorbents.

<table>
<thead>
<tr>
<th>Initial Concns (mg/l)</th>
<th>Ce</th>
<th>$q_e$ (mg/g)</th>
<th>log Ce</th>
<th>Log$q_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.242</td>
<td>4.09</td>
<td>-0.6162</td>
<td>0.6117</td>
</tr>
<tr>
<td>100</td>
<td>0.326</td>
<td>6.32</td>
<td>-0.4868</td>
<td>0.8007</td>
</tr>
<tr>
<td>150</td>
<td>0.352</td>
<td>14.65</td>
<td>-0.4535</td>
<td>1.1658</td>
</tr>
<tr>
<td>200</td>
<td>0.414</td>
<td>335.08</td>
<td>-0.3830</td>
<td>2.5251</td>
</tr>
</tbody>
</table>

**Figure 10.0**: Freundlich isotherm plot for adsorption of Pb (II) onto MCSAC

**3.7.3 Temkin isotherm**

The plot of this isotherm is shown in Figure 11.0. The correlation coefficients $R^2 = 0.505$ for Temkin isotherm are lower than those of Langmuir and Freundlich isotherm constants. So the adsorption characteristic of Pb$^{2+}$ onto MCSAC cannot be represented by Temkin model.

**Table 10.0**: Equilibrium experimental datas for Temkin investigation of Pb (II) ions per unit gram of MCSAC adsorbents.

<table>
<thead>
<tr>
<th>Initial Concns (mg/l)</th>
<th>Ce</th>
<th>$q_e$ (mg/g)</th>
<th>lnCe</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.242</td>
<td>4.09</td>
<td>-1.4188</td>
</tr>
<tr>
<td>100</td>
<td>0.326</td>
<td>6.32</td>
<td>-1.1209</td>
</tr>
<tr>
<td>150</td>
<td>0.352</td>
<td>14.65</td>
<td>-1.0441</td>
</tr>
<tr>
<td>200</td>
<td>0.414</td>
<td>335.08</td>
<td>-0.8819</td>
</tr>
</tbody>
</table>
3.7.4 Harkins-Jura isotherm

The Harkins-Jura isotherm parameters ($A_{HJ}$ and $B_{HJ}$) in Table 12.0 were obtained from the slope and the intercept of the plot of $1/q_e^2$ versus $\log C_e$ respectively [31], as shown in Figure 12.0. The linear correlation coefficient of this isotherm $R^2 (= 0.945)$ showed better fit for the adsorption data than the Langmuir, Freundlich and Temkin isotherms models.

**Table 11.0:** Equilibrium experimental data for Harkin-Jura investigation of Pb (II) ions per unit gram of MCSAC adsorbents

<table>
<thead>
<tr>
<th>Initial Concns (mg/l)</th>
<th>$C_e$</th>
<th>$q_e$ (mg/g)</th>
<th>log $C_e$</th>
<th>$1/q_e^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.242</td>
<td>4.09</td>
<td>-0.6162</td>
<td>0.0598</td>
</tr>
<tr>
<td>100</td>
<td>0.326</td>
<td>6.32</td>
<td>-0.4868</td>
<td>0.0250</td>
</tr>
<tr>
<td>150</td>
<td>0.352</td>
<td>14.65</td>
<td>-0.4535</td>
<td>0.0047</td>
</tr>
<tr>
<td>200</td>
<td>0.414</td>
<td>335.08</td>
<td>-0.3830</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

![Figure 11.0: Temkin isotherm plot for adsorption of Pb (II) onto MCSAC](image1)

![Figure 12.0: Harkin-Jura isotherm plot for adsorption of Pb (II) onto MCSAC](image2)
**3.8 Adsorption kinetics**

From Table 13.0, taking negative logarithm of \((q_e - q_t)\) is undefined, and may seem very difficult to obtain since negative differences (values) of equilibrium adsorption capacity \((q_e - q_t)\) between the experiment and calculation was observed, indicating a poor pseudo first-order fit to the experimental data. And examination of the data shows that the pseudo-first-order kinetic model is not applicable to Pb(II) adsorption onto MCSAC. However, Pseudo-second order show greater correlation coefficient \(R^2\)=1, this shows the applicability of the second-order kinetic model as seen in Table 14.0 and Figure 13.0.

**Table 13.0:** Adsorption kinetic parameters for Pb\(^{2+}\) adsorption onto MCSAC adsorbent \((C_0 =200\ \text{mg/l})\)

<table>
<thead>
<tr>
<th>Contact Time, t (min)</th>
<th>(q_t) (mg/g)</th>
<th>(q_e) (mg/g)</th>
<th>((q_e - q_t)) (mg/g)</th>
<th>(t/q_t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1675.60</td>
<td>335.08</td>
<td>-1340.52</td>
<td>0.0030</td>
</tr>
<tr>
<td>10</td>
<td>1676.10</td>
<td>335.08</td>
<td>-1341.02</td>
<td>0.0060</td>
</tr>
<tr>
<td>15</td>
<td>1683.60</td>
<td>335.08</td>
<td>-1348.52</td>
<td>0.0089</td>
</tr>
<tr>
<td>20</td>
<td>1681.10</td>
<td>335.08</td>
<td>-1346.02</td>
<td>0.0119</td>
</tr>
</tbody>
</table>

**Figure 13.0:** Pseudo-Second-Order kinetic plots for the adsorption of Pb(II) onto MCSAC

**Table 14.0:** Kinetic parameters for Pb\(^{2+}\) adsorption onto MCSAC adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(K_2) (gmg(^{-1})min(^{-1}))</td>
<td>(q_e) (mg/g)</td>
</tr>
<tr>
<td>MCSAC</td>
<td>0.100</td>
<td>333.000</td>
</tr>
</tbody>
</table>

Negative Log \((q_e - q_t)\) undefined
IV. Conclusion

In this study, introducing inorganic polymer on the activated carbon improves the physical properties of activated carbon, adds more functional groups like amine, carboxyl and hydroxyl group on the surface of the adsorbent 40, as identified by FT-IR analysis. Also, SEM and EDX showed clear image size of the pores and elemental composition of the adsorbent before and after modification. The equilibrium results obtained agree with the findings that the effectiveness of Pb(II) ion adsorption under optimized conditions (concentration 200 mg/L, contact time 15 min, dosage 0.2 g/10ml, temperature 20 °C, pH 8) strongly dependent on the quality improvement of the adsorbents. Thus, the result support that coconut shell activated carbon modified with urea immobilized polysiloxane has successfully removed some lead (II) from contaminated water. The amount of metal ion adsorbed increased with increase in concentration and pH of the medium. The isotherms such as Langmuir, Freundlich, temkin and Harkins-Jura models were studied and Harkins-Jura model was found to be in good agreement with experimental data (higher value of coefficients of determination R² =0.945). The kinetic study showed the best fitness of pseudo-second-order model on experimental data.

References


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[47] Ibrahim, M.B. and Sani, S., Comparative isotherms studies on adsorptive removal of congo red from wastewater by watermelon rinds and neem-tree leaves. Open journal of physical chemistry. 2014;4:139-146.