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MODIFICATION OF COCONUT SHELL ACTIVATED CARBON WITH AN AZO LIGAND (DDPTP) FOR ENHANCED REMOVAL OF PB^{2+} FROM CONTAMINATED WATER

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ABSTRACT

The modification of coconut (Cocos nucicera L.) shell activated carbon using an Azo ligand, specifically 1,2–dihydro-1,5-dimethyl-2-phenyl-4-(E)–(2,3,4-trihydrophenyl)-3H-pyrazol-3-one (DDPTP), and its efficacy in removing Pb^{2+} from contaminated water samples was investigated. Proximate analysis revealed moisture content (8.7%), volatile matter (10.4%), ash (3.2%), and fixed carbon (77.7%). The modified adsorbent showed bulk density of 0.46 g/cm³, pore volume of 8.0×10^{-3} cm³, and conductivity of 37.9 µS/cm. FTIR confirmed hydroxyl, carbonyl, amino, and azo functional groups. SEM revealed micro-pores, and EDX showed carbon as the predominant element (57%). The modified activated carbon achieved 98% Pb^{2+} removal, significantly higher than unmodified carbon (79%). Adsorption increased with initial concentration, contact time, carbonization temperature, and pH up to optimal levels, but decreased with larger particle sizes. Optimal ligand loading was 30 mg per 5 g adsorbent. Adsorption data fitted Langmuir, Freundlich, and Temkin isotherms, with kinetics following pseudo-first-order, pseudo-second-order, and intra-particle diffusion models. In light of these results, it can be concluded that modified coconut shell activated carbon is an effective adsorbent, and its adsorption capacity could be further enhanced by incorporating an azo ligand in the appropriate proportions, potentially utilizing an adsorbent to ligand ratio of (5g:25mg).

Keywords: Coconut Shell, Activated Carbon, Azo Ligand, Pb^{2+}, Contaminated Water

INTRODUCTION

Water pollution remains one of the most pressing environmental concerns of the modern world, with heavy metal contamination being a major contributor to the global water crisis. Among the various heavy metals, lead (Pb^{2+}) stands out as a particularly toxic pollutant, posing significant risks to human health and the environment (Addo et al., 2011). Exposure to lead can lead to a wide range of adverse health effects, including neurotoxic damage, kidney dysfunction, and developmental delays in children. Lead contamination primarily occurs through industrial discharge, agricultural runoff, and the degradation of lead-containing materials, necessitating effective and sustainable solutions for its removal from contaminated water sources. In recent years, the removal of toxic heavy metals from water has become a central focus of environmental research. Various methods, including chemical precipitation, ion exchange, and membrane filtration, have been explored for this purpose. However, these methods often suffer from limitations such as high operational costs, generation of secondary pollutants, and insufficient removal efficiency. As a result, there has been a growing interest in alternative, more sustainable approaches, such as the use of adsorbents, which offer advantages like cost-effectiveness, ease of operation, and the ability to target specific pollutants. One such promising adsorbent is activated carbon (AC), which is widely used due to its high surface area, porous structure, and ability to adsorb a wide range of contaminants, including heavy metals. Activated carbon is typically derived from various organic materials, such as coal, peat, wood, and agricultural by-products. Among these, coconut shell-derived activated carbon (CSAC) has gained attention due to its renewable nature, low cost, and exceptional adsorption properties. However, despite its advantages, the efficiency of CSAC in removing certain pollutants, such as lead ions, can be limited, especially when compared to more expensive adsorbents or complex treatment methods. To enhance the performance of coconut shell activated carbon (CSAC), various modification techniques have been explored, including physical and chemical treatments, which improve its adsorption capacity and specificity toward particular contaminants (Itodo et al., 2021). One such modification involves the use of ligands, which are molecules that can bind to metal ions and enhance the adsorption process. Ligands, particularly those with chelating properties, can form stable complexes with metal ions, improving the overall removal efficiency. A promising class of ligands that has shown potential in enhancing adsorption capacity are azo compounds, which contain the functional -N=N- group known for its ability to bind to metal ions. Among the vast array of azo compounds, the azo ligand 1,2-Dihydro-1,5-Dimethyl-2-Phenyl-4-(E)-(2,3,4-Trihydroxyphenyl)-3H-Pyrazol-3-One (DDPTP) has been identified as a potentially effective ligand for modifying activated carbon to remove lead ions from contaminated water. DDPTP is a pyrazolone-based ligand containing both hydroxyl and phenyl groups, which can facilitate the formation of strong complexes with metal ions such as Pb^{2+}. The inclusion of DDPTP in the modification of CSAC could potentially enhance the sorbent's affinity for lead ions, leading to a more efficient and selective removal process (Aglanu & Appiah, 2014). The modification of activated carbon using azo ligands such as DDPTP offers a dual benefit: the inherent adsorptive properties of CSAC are enhanced, while the ligand can provide selective binding sites for Pb^{2+} ions. This approach not only improves the removal efficiency of lead from water but also allows for the development of a more sustainable solution for heavy metal contamination. Moreover, the modification process may open up new avenues for the use of activated carbon in removing other pollutants from water, thereby broadening its application in environmental remediation. By focusing on this specific modification, the study seeks to contribute to the development of more efficient and cost-effective materials for water treatment. The study will examine the synthesis of the modified adsorbent, characterize its surface properties, and evaluate its adsorption capacity and kinetics for Pb^{2+} removal. The findings could provide valuable insights into the potential of DDPTP-modified coconut shell activated carbon as a viable solution for mitigating lead contamination in water (Erienu et al., 2022).

This research aims to explore the modification of coconut shell activated carbon using the azo ligand 1,2-Dihydro-1,5-Dimethyl-2-Phenyl-4-(E)-(2,3,4-Trihydroxyphenyl)-3H-Pyrazol-3-One (DDPTP) and to assess its effectiveness in the removal of Pb^{2+} from contaminated water.

MATERIALS AND METHODS

Materials

All chemicals utilized in this research were of reagent grade and did not require any additional treatment. The analytical reagent grade nitrate salts of lead were employed without any further purification. Approximately 100 mg/l aqueous solutions of Pb^{2+} ions were prepared as stock solutions from their respective salts [$Pb(NO_3)_2$]

Synthesis of the Ligand

The ligand synthesis was conducted following the methodologies outlined by Bentum et al. (2011) and Obruche et al. (2019). Reagent grade chemicals were utilized without any additional purification. The azo ligand, 1,2-dihydro-1,5-dimethyl-2-phenyl-4(E)-(2,3,4-trihydroxyphenyl)-3H-pyrazol-3-one, referred to as DDPTP, was synthesized according to the procedure established by Heinosuke Yasuda. This involved dissolving 0.1218 g of 4-aminoantipyrine (the amine) in dilute hydrochloric acid (1 cm^3 of concentrated HCl in 5 cm^3 of distilled water), followed by diazotization of the resulting solution with sodium nitrite (0.06 g of $NaNO_2$ in 2 cm^3 of water) at temperatures below 5 °C while using magnetic stirrer.

The diazotized 4-aminoantipyrine, which exhibited a purple hue, was introduced into a solution containing 1,2,3-trihydroxylbenzene (0.0882 g) and sodium acetate (2.5 g) dissolved in 30 cm3 of distilled water. This mixture was subjected to mechanical stirring at room temperature. The resultant product, which appeared brown, was subsequently collected and washed with a methanol/ethanol mixture in water. To achieve a more purified ligand, the compound underwent recrystallization in dichloromethane and was then stored in desiccators over $CaCl_2$.

Preparation of Coconut Shells

The procedures for preparing coconut shells were akin to those described by Oram (2014) and Ekpo et al. (2023), albeit with some minor modifications. Coconut fruits were procured from Oba Market in Nsukka, selectively chosen, and the endosperm (copra) was separated from the shell. The coconut shells (coir) were immersed in water for one hour before being thoroughly cleaned with a sponge to eliminate dirt and residual grease. They were then dried in an oven (OV-160) at 105 °C for 1 hour. The dried shells were subsequently shattered into fragments using a hammer on a clean surface. These fragments were ground into fine particles using a grinding machine, and various sieve sizes were employed to achieve different particle sizes, specifically 0.25, 0.5, 1.4, and 2.8 mm.

Figure 1: Coconut Shell

Carbonization and Activation (Chemical Activation)

The ground samples with particle sizes of 0.25, 0.5, 1.4, and 2.8 mm were subjected to carbonization in a Vaster Chesterfield Furnace, Model L F 3, at a temperature of 400 °C for a duration of 1 hour. Subsequently, the carbonization process was repeated using the 0.25 mm adsorbent at different temperatures: 300 °C, 350 °C, and 450 °C. The carbonized coir samples underwent activation with calcium carbonate ($CaCO_3$). Approximately 10 g of $CaCO_3$ was dissolved in 50 cm^3 of distilled water within a 100 cm^3 beaker. This solution was then combined with 50 g of carbonized coir and allowed to sit for 24 hours, facilitating the opening of the pores. After 24 hours, the mixture was filtered and initially washed with 0.5 M acetic acid, followed by rinsing with de-ionized water until the pH reached approximately 7. The samples were then dried at 110 °C for 3 hours and stored in an airtight container (Obruche et al., 2028).

Modification was Performed using the Azo Ligand; 1,2-dihydro-1,5-dimethyl-2-phenyl-4(E)-(2,3,4-trihydroxyphenyl)-3H-pyrazol-3-one, referred to as DDPTP

A 30 mg quantity of the azo ligand was dissolved in 2 cm³ of methanol and subsequently diluted with 50 cm³ of de-ionized water. A 5 g sample of activated carbon (CSAC) was stirred with a 0.06% DDPTP solution (30 mg in 50 cm³) using a mechanical shaker, Multi-fix (M80), for 30 minutes. The resulting solution was allowed to stand for 24 hours before being dried at 60 °C for 1 hour in an oven. Additionally, four other samples, each weighing 5 g of CSAC, were modified with varying amounts of the ligand: 10 mg, 20 mg, 40 mg, and 50 mg, to assess the impact of ligand quantity on the adsorption of metal ions (Ekpo et al., 2023).

Analysis

Determination of the Moisture Content, pH, bulk Density, Ash Content, Pore Volume, Volatile Matter and fixed Carbon

Analysis involved the determination of moisture content, pH, bulk density, ash content, pore volume, volatile matter, and fixed carbon. These parameters were assessed following the standard methods established by the USEPA (1987). The fixed carbon content is calculated by subtracting the total percentages of ash, volatile matter, and moisture content from 100, as outlined by the USEPA standard. This is expressed as follows:

Fixed carbon % = 100 – moisture % - ash % - volatile matter % (1)

Adsorption Procedure

Batch adsorption experiments were conducted to examine how initial metal ion concentration, contact time, particle sizes, solution pH, ligand concentration, and carbonization temperature affect the adsorption of Pb^{2+} on MCSAC. Adsorption studies utilized 25 cm^3 of each metal ion solution along with 0.5 g of the adsorbent. After each experiment, the contents of each tube were filtered through Whatman filter paper, and the concentration of residual metal ions in each filtrate was measured using AAS. All experiments were meticulously performed to ensure accurate results. The measurement of metal ions was carried out with a Bulk Scientific 210VGP atomic absorption spectrometer (AAS) that had a hollow cathode lamp and a deuterium background corrector, using air-acetylene flame at the appropriate wavelengths. A pocket-sized pH meter (pHep) was employed to adjust the pH of the test solutions. The data collected were analyzed using the Langmuir and Freundlich isotherms. The removal efficiency was calculated by determining the percentage sorption using the equation 2.

% Absorption = Ci-Ce /Ci x 100 (2)

Where;

Ci = initial concentration before adsorption (mg/L)

Ce = concentration after adsorption (mg/L)

Variation of Initial Metal Ion Concentration

Batch adsorption was conducted utilizing initial metal ion concentrations of 0.5, 1.0, 2.0, 3.0, and 4.0 mg/l for the aqueous solution of Pb^{2+} ions. Subsequently, 0.5 g of the adsorbent (MCSAC) was accurately weighed into five (120 cm3) bottles, into which 25 cm3 of each initial concentration of the metal solution was added. This procedure was replicated for the three different metal ions. The adsorption mixtures were agitated uniformly and continuously using a mechanical shaker for duration of 30 minutes, after which the contents of each beaker were filtered into clean sample bottles. The concentration of residual metal ions in the filtrates was assessed using Atomic Absorption Spectroscopy (AAS). The quantity of metal ions adsorbed from the solution was calculated by determining the difference in concentration (USEPA, 2004).

Variation of Contact Time

The adsorption of metal ions onto MCSAC was examined over various time intervals (10, 30, 50, 70, and 90 minutes). From the working solutions, 25 cm^3 of metal ions were dispensed into five labeled bottles, each containing 0.5 g of the adsorbent. The mixtures were agitated uniformly for 30 minutes. This experimental setup was subsequently repeated for all the metals. At the conclusion of each contact time, the contents of each sample were filtered. The concentration of metal ions was determined (USEPA, 2004).

Variation of Temperature of Carbonization

The adsorption of metal ions onto MCSAC was investigated at various activation temperatures (300, 350, 400, and 450 °C). From the working solutions, 25 cm^3 of metal ion solutions were measured into four labeled bottles, each containing 0.5 g of the adsorbent. The mixtures were agitated uniformly for 30 minutes. The experimental setup was repeated for the three metal solutions. At the end of each contact time, the contents of each beaker were filtered, and the residual concentration of metal ions in the filtrates was determined using AAS, with the amount of metal ions adsorbed calculated (USEPA, 2004).

Variation of pH Value

The adsorption of metal ions onto MCSAC was investigated at different pH levels (2, 4, 6, 8, and 10). The adsorption experiments utilized 25 cm3 of each metal ion solution with an initial concentration of 0.5 mg/L. The metal ion solutions were distributed into five labeled bottles, each containing 0.5 g of the adsorbent (this procedure was repeated for the three metal ion solutions). The mixtures were agitated uniformly for 30 minutes. Upon completion of each pH analysis, the contents of each tube were filtered. The concentration of metal ions in the filtrates was measured using an AAS, and the quantity of metal ions adsorbed was calculated (USEPA, 2004).

Variation of Particle Size

The adsorption of metal ions onto MCSAC was examined at various particle sizes: 0.25, 0.5, 1.4, and 2.8 mm. The adsorption studies were conducted using 25 cm3 of each metal ion solution with an initial concentration of 0.5 mg/L. The metal ion solutions were allocated into four labeled bottles, each containing 0.5 g of the adsorbent (this was repeated for the three metal ion solutions). The mixtures were uniformly agitated for 30 minutes. After this period, the contents of each tube were filtered. The concentration of metal ions in the filtrates was determined using an AAS, and the amount of metal ions adsorbed was calculated (USEPA, 1987).

Variation of Ligand Amount

The adsorption of metal ions was investigated on CSAC modified with varying amounts of ligands, specifically DDPTP. This was performed using 25 cm^3 of metal ion solutions, which were measured into five labeled bottles, each containing 0.5 g of the adsorbent modified with different amounts of DDPTP (10, 20, 30, 40, and 50 mg). The mixtures were uniformly agitated using a mechanical shaker for 30 minutes. The experimental setup was subsequently repeated for all the metals. At the conclusion of each contact period, the contents of each container were subjected to filtration. The concentration of metal ions present in the filtrates (those that were not adsorbed) was measured using Atomic Absorption Spectroscopy (AAS), and the quantity of metal ions that were adsorbed was calculated by taking the difference. This procedure was repeated for all three metals.

Variation in the Level of Treatment of the Adsorbent on Adsorption

The adsorption of metal ions onto MCSAC was investigated using various types of adsorbents: uncarbonized (A), carbonized unactivated (B), activated unmodified (C), and modified (D) adsorbents. The adsorption experiments were conducted with 25 cm^3 of each metal ion solution, which had an initial concentration of 0.5 mg/l and a pH of 7.5. The metal ion solutions were dispensed into four labeled bottles, each containing 0.5 g of the respective adsorbent (this was repeated for the three metal ion solutions). The mixtures were agitated uniformly for 30 minutes using a mechanical shaker. After this period, the contents of each tube were filtered. The concentration of metal ions in the filtrates was determined using AAS, and the amount of metal ions that were adsorbed was calculated (USEPA, 2004).

Quality Control

Before analysis of the samples, standards and blanks were run to check the calibration of the instrument. Laboratory blanks and standards were primarily used to check contaminations and precisions, respectively, of the analytes. The quality assurance measures also included strict cleansing of laboratory glassware.

Statistical Data Analysis and Precision

All assessments of heavy metals and polycyclic aromatic hydrocarbons were conducted in triplicate, with results expressed as mean ± standard deviation to evaluate the precision of the measuring instruments. This precision reflects the closeness of the results from replicate samples or indicates the reproducibility of findings obtained under identical conditions. The SPSS version 20 software was employed to compute the mean values from the triplicate data, ascertain the standard deviation, and perform analysis of variance (ANOVA) at a significance threshold of less than 0.05 ($P<0.05$). Furthermore, Principal Component Analysis (PCA) was executed based on the Pearson Correlation matrix analysis and component plot in rotated space statistics (Obruche et al., 2019).

RESULTS AND DISCUSSION

This section presents the analyzed results regarding the modification of coconut shell activated carbon with the azo ligand 1,2-Dihydro-1,5-Dimethyl-2-Phenyl-4-(E)-(2,3,4-Trihydroxyphenyl)-3H-Pyrazol-3-One (DDPTP) and evaluates its effectiveness in removing Pb^{2+} from contaminated water, as illustrated in Tables 1-13.

Physical Characterization and Molar Conductivity Data of the Ligand.

The azo ligand, 1,2-dihydro-1,5-dimethyl-2-phenyl-4-[E]-(2,3,4-trihydroxylphenyl)-3H-pyrazol-3-one (DDPTP), was characterized, and the following results were obtained. From Table 1, it was noted that the ligand's molar conductivity was significantly higher than the instrumental range for non-conductors, which is between 0 and 0.3 μScm^{-1}. The ligand exhibited some conducting characteristics, likely because of dissociations happening in its solution.

Table 1: Physical Characteristics and Molar Conductivity Data of the Ligand

Compound	Colour	Texture	Melting	Yield	% yield	Molar conductivity
Ligand	Dark brown	Powdery	190	0.35	35.40	26.10

Physico-Chemical Properties of the Adsorbent

The physical and chemical properties of the adsorbent are presented in Table 2.

Table 2: Physico-Chemical Properties of the Adsorbent

Parameters	Result
colour	Black
pH	8.6
Conductivity (1%)	37.9µS/cm
Pore volume	8.0x10-3cm3
Fixed carbon	77.7%
Moisture content	8.7%
Volatile matter	10.4%
Ash content	3.2%
Bulk density	0.46g/cm3

The adsorbent that was developed underwent characterization using Fourier Transform Infrared Spectroscopy (FTIR), which revealed the existence of certain functional groups (Figures 2-4) that play a role in the adsorption of metal ions. It was noted that the activated unmodified carbon lacks free –OH groups and azo groups (-N=N-) in its composition, in contrast to the modified carbon and the adsorbed carbon. The presence of the azo group was detected in both the modified carbon and the adsorbed carbon (Figures 2&3) due to their modification with an azo ligand. The porous characteristics of the adsorbent were demonstrated through Scanning Electron Microscopy (SEM) as illustrated in figure 5. The SEM analysis indicates the formation of micropores resulting from the carbonization process of the adsorbent. These findings align with the research conducted by Olowu et al. (2010) and Obruche et al. (2019) concerning the adsorption of heavy metals in the same field and Energy Dispersive X- ray (EDX) spectrum shows the percentage of atoms in the adsorbent with carbon as the major quantitative elements.

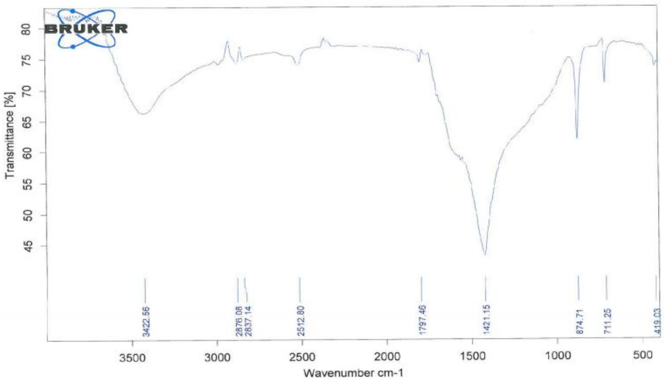

Figure 2: FTIR of Unmodified CSAC before Adsorption

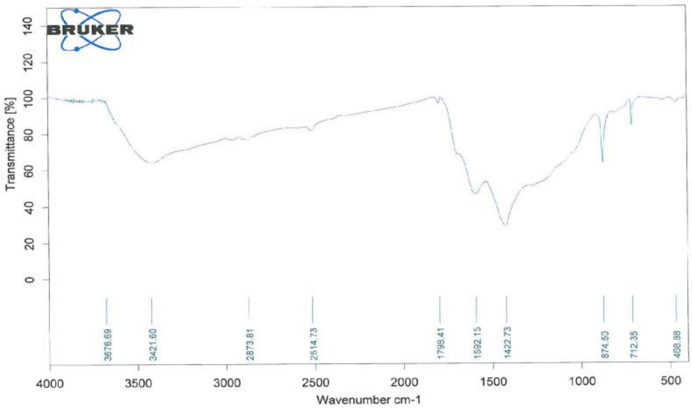

Figure 3: FTIR of MCSAC before Adsorption

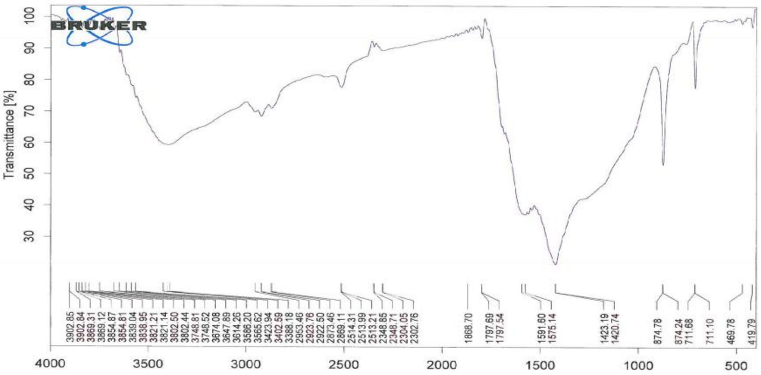

Figure 4: FTIR of MCSAC after Adsorption of Pb^{2+}

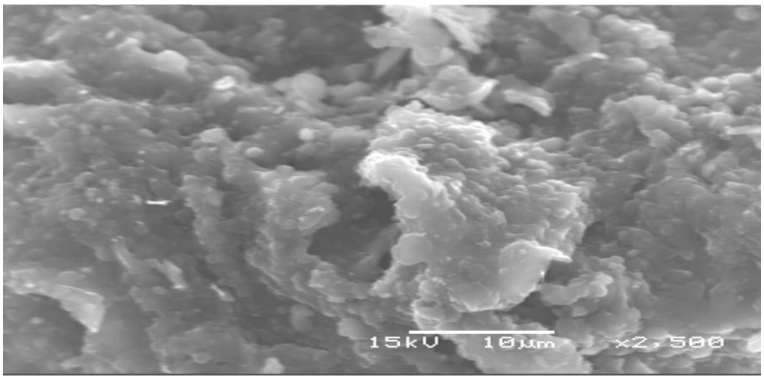

Figure 5: SEM Image for MCSAC

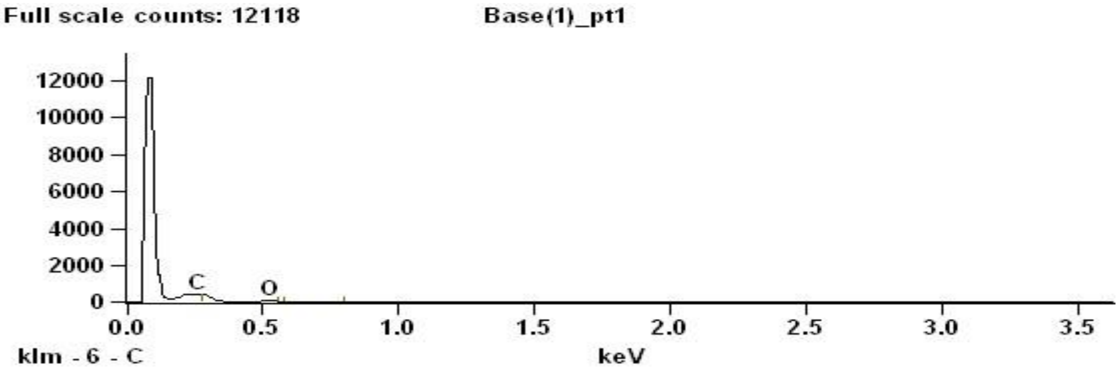

Figure 6: Energy Dispersive X-ray Spectrum of MCSAC

Adsorption

Impact of Concentration on the Removal of Pb^{2+} from Solutions

The influence of the initial concentration of metal ions on the amount of metal ions adsorbed, Qe (mg/l), by MCSAC was examined at room temperature. It was observed that the quantity of metal ions adsorbed, Qe (mg/l), increased with a rise in the initial concentration of metal ions, as illustrated in Table 3. This phenomenon occurs because, as the initial concentration increases, a greater number of metal ions become available in the solution for the adsorption process. The adsorption of metal ions escalates with an increase in metal ion concentration since, at lower concentrations; the active sites on the adsorbent's surface are not fully occupied, allowing for a higher likelihood of additional ions being adsorbed with the increase in initial concentration. These findings are consistent with the studies conducted by Oduro et al. (2001) and Umudi et al. (2025) regarding plant adsorption.

Table 3: Concentration of the Pb2+ Ions Adsorbed (Qe) at Various Concentration at Room Temperature and pH 7.5 by MCSAC

Initial Concentration Co (mg/l)	Pb2+	%Removal of Pb2+
0.5	0.452	90.40
1	0.939	93.90
2	1.923	96.15
3	2.891	96.37
4	3.702	92.55

Impact of Contact Duration on the Removal of Pb^{2+} from Solutions

The adsorption behavior of Pb2+ on MCSAC was examined over time to determine the equilibrium duration necessary for optimal adsorption of metallic ions. Table 4 illustrates the adsorption levels of the metal ions utilizing MCSAC. It was noted that the quantity of metal ions adsorbed onto the MCSAC increased with prolonged agitation time. This phenomenon can be attributed to the migration of a greater proportion of metal ions from the bulk solution through the adsorbent boundary layer to the active sites of the adsorbent as time advances. The increased sorption of the metal ion with extended agitation time may result from a reduction in boundary layer resistance to mass transfer in the bulk solution, along with an elevation in the kinetic energy of the hydrated metal ions68. The removal of metal ions by MCSAC may also stem from variations in sorption mechanisms: ion-exchange, adsorption (physisorption/chemisorption), coordination, and complexation due to the diverse types of ion-binding groups such as hydroxyl, carboxylic, and phenolic functional groups present in MCSAC (Ogwuche and Obruche, 2020).

Table 4: % Removal of the Metal Ions Adsorbed (Qe) at Various Time Interval at Room Temperature and Ph 7.5 by the Adsorbent (Mcsac)

Time(min)	% Removal of Metal Ions, Qe
	Pb2+
10	30.4
30	46.2
50	70.8
70	80.2
90	88.4

The initial rapid rate may be attributed to the availability of the exposed surface area of the adsorbents, as the kinetics of adsorption is influenced by the surface area of the adsorbents. As these sites become increasingly occupied, the sorption process becomes more challenging, and the overall sorption process tends to become less favorable. This represents the general characteristics of metal ion adsorption.

Impact of Carbonization Temperature on the Sorption Capacity of the Adsorbent

Temperature can influence the adsorption behavior of metallic ions in solution. The impact of carbonization temperature on the adsorption of Pb^{2+} from solutions containing MCSAC was examined at an initial concentration of 0.5 mg/l over a contact time of 30 minutes at room temperature. Table 5 indicates that the removal of Pb^{2+} from the aqueous solution by MCSAC was contingent upon the carbonization temperature. An increase in carbonization temperature from 300°C to 450°C resulted in a consistent rise in the removal of metal ions by the adsorbent. This suggests that a higher carbonization temperature leads to a larger surface area of the adsorbent available for adsorption. This phenomenon is attributed to the reduction in the size of the adsorbent particles as the carbonization temperature escalates. These findings align with the research conducted by (Ugochukwu et al., 2025) in the same field.

Table 5: % Removal of the Pb2+Adsorbed (Qe) at Various Temperature, pH7.5 by Coconut (MCSAC)

Temperature (oC)	% Removal of Metal Ions Pb2+
300	68
350	78.2
400	84
450	90

Impact of pH on the Extraction of Pb2+ from Solution

The pH level serves as a crucial controlling factor for the adsorption of metal ions, as it influences the solubility of these ions, the concentration of counter ions on the adsorbent's functional groups, and the degree of ionization of the adsorbate during the reaction. In highly acidic conditions, heavy metal cations are entirely released. At lower pH levels, H^+ ions compete with metal cations for adsorption sites within the system. The influence of pH on the adsorption of Pb^{2+} using MCSAC was examined at an initial concentration of 0.5 mg/L over duration of 30 minutes at room temperature. Table 6 indicates that the concentration of metal ions rises as the pH transitions from acidic (pH 2) to alkaline (pH 10). This finding illustrates the effect of pH on the adsorption of metal ions by MCSAC. Furthermore, Table 6 reveals that an alkaline environment promotes adsorption more effectively than an acidic one. As the pH of the solution increases, metal hydrolysis and precipitation commence, with the onset of adsorption occurring prior to the initiation of hydrolysis.

Table 6: % Removal of the Pb^{2+} Adsorbed at Various pH at Room Temperature by MCSAC

pH	% Removal of Metal Ions Pb2+
2	53.6
4	63.4
6	90.4
8	90
10	88

When the pH of the adsorbing medium was raised from pH 2 to 10, there was a notable increase in the deprotonation of the adsorbent surface, resulting in a reduction of hydrogen ions present on the adsorbent surface. This phenomenon generates a greater number of negative charges on the adsorbent surface, which enhances the adsorption of positively charged species and the positive sites on the adsorbent surface. The hydrolysis of cations transpires through the substitution of metal ligands within the inner coordination sphere with hydroxyl groups. This substitution takes place following the removal of the outer hydration sphere surrounding the metal cations. The findings obtained were consistent with the observations made by several researchers. It is well-established that the solubility of metals diminishes at elevated pH levels (specifically at pH > 8) (Umanah et al., 2025).

Effect of Degree of Treatment of Adsorbent (MCSAC)

As the degree of treatment of the adsorbent increased, it was noted from the percentage removal in table 7 that the amount of metal ions adsorbed from the solution rose for all three metals. This increase can be attributed to the enhanced adsorption capacity achieved through the carbonization of the adsorbent (which improves pore volumes and surface structure), activation with an activating agent, $CaCO^3$ (which not only enhances the surface structure but also improves the functional groups of the adsorbent), and modification with DDPTP (which introduces additional functional groups such as amine and hydroxyl groups onto the surface of the adsorbent) (Festus-Amadi et al., 2021).

Table 7: % Removal of the Metals Ions Adsorbed at Various Levels of Treatment Room Temperature and pH. 7.5

Degree of Treatment of Adsorbent	% Removal of Pb2+
A	20.4
B	35.6
C	79
D	98

Impact of Ligand Quantity on Pb2+ Adsorption

The influence of ligand concentration was examined, revealing that the amount adsorbed peaked at 30 mg of the ligand. Beyond this point, a decline in the adsorbed quantity was noted, likely due to the development of charged complexes that could not be fully retained on the solid phase7. Table 8 illustrates the changes in the percentage removal of metal ions in relation to the amount of ligand utilized for the modification of the adsorbent (Umudi et al., 2025).

Table 8: % Removal of the pb^{2+} Adsorbed at Various Amount of Ligand at Room Temperature and pH 7.5

Amount of Ligand (mg)	% Removal of Pb2+, Qe
10	66.2
20	72
30	85.6
40	66
50	61

Impact of Particle Size on the Adsorption of Pb2+

The dimensions of an adsorbent's particles significantly influence its surface area; specifically, smaller particle sizes result in a larger surface area. This increase in surface area provides additional adsorption sites for metal ions, facilitating greater adsorption. Conversely, larger particle sizes lead to a reduction in surface area, thereby diminishing the amount of metal ions that can be adsorbed. This phenomenon is illustrated in Table 9 (Obruche et al., 2019).

Table 9: % Removal of the Metal Ions Adsorbed at Various

Particle Sizes (mm)	% Removal of Pb2+
0.25	96
0.5	80
1.4	68.2
2.8	22

Particle Sizes of MCSAC at Room Temperature and pH 7.5

Adsorption Isotherm

The Langmuir Isotherm

The Langmuir model operates under the premise that maximum adsorption is achieved when a saturated monolayer of solute molecules exists on the surface of the adsorbent. This research determined the maximum monolayer coverage capacity (Qm) from the Langmuir isotherm model to be 0.164, -2.74, and 3.086 mg/g for lead, cadmium, and nickel, respectively. The Langmuir isotherm constant (KL) and the separation factor (RL), as presented in Table 10, indicate that the equilibrium sorption was favorable, with the exception of cadmium. The R^2 value demonstrated that the sorption data aligned well with the Langmuir Isotherm model solely for lead.

Table 10: Isotherm Data for Langmuir and its Constants

		Pb2+			
C0 (mg/l)	1/Qe (g/mg)	1/C (1/mg)	Constants, KL (L/mg)	RL	R^2
0.5	2.2124	20.8333	0.924	0.924	0.774
1.0	1.065	16.3934			
2.0	0.52	12.987			
3.0	0.3459	9.1743			
4.0	0.2701	3.3557			

The Freundlich Isotherm

The Freundlich adsorption isotherm describes the correlation between the quantity of metal adsorbed per unit mass of adsorbent, denoted as Qe, and the concentration of the metal at equilibrium, referred to as Ce. The data pertaining to the Freundlich adsorption isotherm, derived from the sorption of lead ions, is presented in table 11.

T able 11: The Freundlich Isotherm and its Constant

		Pb2+			
C0 (mg/l)	LogCe	LogQe	Constants, n	Kf(mg/g)	R^2
0.5	-1.319	-0.344	0.924	17.66	0.731
1.0	-1.215	-0.027			
2.0	-1.114	0.284			
3.0	-0.963	0.461			
4.0	-0.526	0.568			

Kinetic Study

To explore the controlling mechanism of adsorption processes, including mass transfer and chemical reactions, the pseudo-first-order and pseudo-second-order equations were utilized to model the kinetics of lead adsorption on MCSAC.

The pseudo-first-order

The pseudo-first-order rate equation, known as the Lagergren equation, is typically represented as:

$$dQt/dt = Ki(Qe-Qt) \quad (3)$$

The linear form is given by:

$$Log(Qe-Qt) = Log(Qe) - Kit/2.303 \quad (4)$$

In this equation, Qt and Qe denote the amount adsorbed (mg/g) at time t and at equilibrium, respectively, while ki represents the rate constant of the pseudo-first-order adsorption process (min^{-1}). Straight line plots of log(Qe-Qt) versus t were employed to ascertain the rate constant, ki, and the correlation coefficients, R^2, for a concentration of 0.5 mg/l of the metal ions. With coefficients of 0.930 and 0.960 for lead, it was observed in Table 12 that the adsorption of lead ions on MCSAC adheres to pseudo-first-order kinetics when compared to the correlation coefficient of pseudo-second-order kinetics.

Table 12: Data for Pseudo-First-Order and Constants

Time (min)	Log(Qe-Qt) Pb2+	Constants Kt (min-1)	Qe (mg/g)	R2
10	-0.5229	0.041	0.634	0.930
30	-0.6556			
50	-1.0088			
70	-1.2924			
90	-2.0000			

The Pseudo-Second-Order Kinetics

The pseudo-second-order kinetics may be expressed as;

dQt/dt = Ki(Qe-Qt) (5)

the linear form is

Log(Qe-Qt) = Log(Qe) – Kit/2.303 (6)

The equilibrium adsorption capacity (Qe) and the second-order constants k2 (gmg-1h-1) can be experimentally determined from the slope and intercept of the plot of t/Qt against t. The initial adsorption rates ho (mg/g min) can be calculated using the pseudo-second-order model with the following equation:

h0 = K2Q 2. E (7)

Here, ho = (mg g^{-1} min^{-1}) is considered the initial adsorption rate at t = 0, and k2 represents the rate constant for pseudo-second-order adsorption (g mg-1min-1). The linearized form plots of the pseudo-second-order reaction at a concentration of 0.5 mg/L for Pb^{2+} using CSAC-M are presented in Table 13.

Table 13: Pseudo-Second-Order Reaction and Constants

Time (min)	t / Qt) Pb2+	Constants K2 (gmg-1 min-1)	Qe (mg/g)	R^2	h0(mgg-1 min-1)
10	192.31	0.041	0.634	0.930	6.61x 10-3
30	129.87				
50	141.24				
70	174.54				
90	203.62				

The pseudo-second-order rate constants have been determined as indicated in table 13, along with the associated correction coefficients. It was noted that lead exhibited an R2 value of 0.930, primarily following the pseudo-second-order reaction model. This finding aligns with the research conducted by Umudi et al. (2025).

CONCLUSION

This research examined the sorption capacity of modified coconut shell activated carbon (MCSAC) for Pb^{2+} ions from contaminated water. The results confirm that coconut shell-derived activated carbon is an effective, cost-efficient adsorbent for removing Pb^{2+} from polluted water. Characterization techniques such as SEM, EDX and FTIR supported these findings. The study showed that Pb^{2+} adsorption increased with higher initial concentrations, longer contact times, elevated carbonization temperatures, and varying pH levels. Particle size and ligand amounts affected removal efficiency. Kinetic studies indicated sorption followed both pseudo-first-order and pseudo-second-order models. Overall, MCSAC is a promising material for wastewater treatment, and its capacity can be enhanced by optimizing the adsorbent-ligand ratio.

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