

Removal of Pb (II) and Cd (II) from Aqueous Solution Using Chitosan Modified Sawdust Char

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Abstract: *It is expedient to remove heavy metals from industrial effluent before releasing to the environment to avoid pollution. This study compared the efficacies of sawdust char (SC) with Chitosan modified sawdust char (MSC) and Activated Carbon (AC) for the adsorptive uptake of Pb (II) and Cd (II) from simulated effluent. Elemental composition analysis using Rutherford backscattering spectrometry (1.7 MeV Tandem Accelerator) revealed the presence of C, K, Ca, Mg, Al, Si, P and Cl as part of the constituent of the adsorbent while morphological characteristic was revealed by Scanning Electron Microscope (SEM). Batch adsorption study was performed with the aim of assessing the uptake of Pb²⁺ and Cd²⁺ under various factors such as initial concentration, adsorbent dosage, pH, and contact time. The natural adsorbents exhibit good uptake for Pb²⁺ and Cd²⁺ at pH 6.8; initial concentration of 20 mg/L; adsorbent dosage of 2 g; and agitation time of 60 min. Experimental data were analysed using adsorption isotherms which showed that the adsorption equilibrium is well-fitted to Langmuir and Freundlich isotherm. The order of metal ion selectivity by the natural adsorbent (modified and unmodified) was: Pb (II) > Cd (II). Sawdust char could be successfully utilized for removal of heavy metals from industrial effluents especially when modified with chitosan, at the same time, solving the problem of disposal of plant waste materials.*

Keywords: *sawdust char, chitosan, heavy metal, adsorption, industrial effluent.*

1. Introduction

Water pollution is unarguably one of the most fundamental environmental issues globally and locally, as untreated or inadequately treated wastes is being discharged into streams, estuaries and seas [1]. Water pollution affects plants and organisms living in bodies of water. In almost all cases the effect is damaging not only to individual species and populations, but also to the natural biological communities [2].

Heavy metal pollution has become a more serious environmental problem in the last several decades as a result of its toxicity and insusceptibility to the environment [3]. Naturally, heavy metals are continuously released into the aquatic environment through processes such as volcanic activity and weathering of rocks. Industrial activities have significantly enhanced the mobilization of heavy metals.

Rapid industrialization has led to increased disposal of heavy metals into the environment [4]. Heavy metals are notorious water pollutants with some having high lethality and carcinogenicity [5]. Their presence in the wastewater of several industrial processes, such as electroplating, metal finishing, metallurgical work, tanning, chemical manufacturing, mining and battery manufacturing, has brought about more environmental concerns due to their toxicity even at low concentrations [3].

Lead (Pb²⁺) interferes with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidneys, and reproductive and nervous systems. It interferes with the development of the nervous system and is therefore particularly toxic to children, causing potentially permanent learning and behaviour disorders. Symptoms include abdominal pain, confusion, headache, anaemia, irritability, and in severe cases seizures, coma, and death.

Humans are commonly exposed to cadmium by inhalation and ingestion. Health effects includes diarrhoea, stomach pains, bone fracture, reproductive failure, damage to the central nervous system and immune system, psychological disorders, etc. Cadmium exposure has also been linked with pulmonary emphysema and possibly bone demineralization [6]. It acts as a mitogen and promotes cancer in a number of tissues. It also stimulates cell proliferation, inhibit DNA repair and inhibit apoptosis.

The undesirable effects of heavy metals pollution can be avoided by treatment of the wastewater prior to discharge [7]. Many methods that are being used to remove heavy metal ions include chemical precipitation, ion-

exchange, adsorption, membrane filtration, electrochemical treatment technologies, etc. [8, 9]. Most conventional methods for heavy metals removal from the wastewater are both expensive and difficult.

Adsorption which is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid (adsorbate) to a surface (adsorbent) is considered as one of the suitable water treatment methods due to its ease of operation and the availability of a wide range of adsorbents. Besides, adsorption can also be applied for the removal of soluble and insoluble organic, inorganic, and biological pollutants in trace concentrations. Adsorption is controlled by various parameters such as temperature, nature of the adsorbate and adsorbent, and the presence of other pollutants along with the experimental conditions (pH, concentration of pollutants, contact time, particle size, and temperature) [4, 10].

Adsorption processes, using industrial activated carbon, have been attempted to remove organic pollutants but the challenge of regenerating the spent adsorbent and the related high cost of the regeneration process have not given the adsorption process the deserved extensive applications [11-13]. Hence, natural materials have been investigated as potential industrial adsorption media. The use of natural adsorbents in wastewater treatment have received increasing attention and currently offer a very attractive method for pollution remediation [14].

Char prepared from agricultural wastes have been used to adsorb organic and inorganic pollutants by some researchers. Activated carbon prepared from peanut hulls, an agricultural waste by-product has been used for the adsorption of cadmium from synthetic wastewater. Peanut hull carbon was found to be an effective adsorbent for the removal and recovery of Cd^{2+} from aqueous solutions; its adsorption capacity being much superior to commercial activated carbon [15]. Chitosan modified adsorbents have shown higher efficiency for heavy metals removal from wastewater.

Chitosan is produced commercially by deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans (such as crabs and shrimp) and cell walls of fungi [16]. A common method for the synthesis of chitosan is the deacetylation of chitin using sodium hydroxide in excess as a reagent and water as a solvent. The reaction occurs in two stages under first-order kinetic control. Activation energy for the first step is higher than the second; its value is an estimated 48.76 kJ/mol at 25-120°C [17]. This reaction pathway, when allowed to go to completion (complete deacetylation) yields up to 98% product [18].

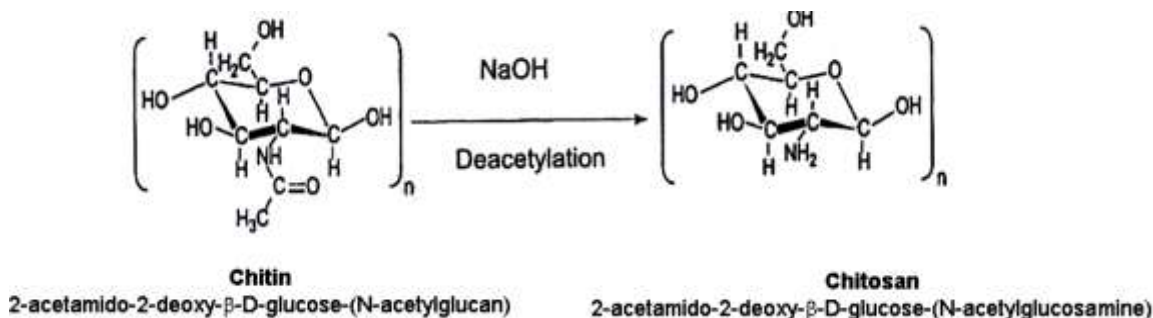


Fig. 1. Conversion of chitin to chitosan by deacetylation.

Chitosan causes the fine sediment particles to bind together, and is subsequently removed with the sediment during sand filtration. It also removes phosphorus, heavy minerals, and oils from the water. Chitosan has been proven to enhance filtration process. Sand filtration can remove up to 50% of effluent turbidity, while sand filtration modified with chitosan can remove up to 99% of same effluent turbidity [19]. The chitosan used for this research was extracted from periwinkle shell. This present article is devoted to study the adsorption efficiency of sawdust modified with chitosan extracted from periwinkle shell for removal of Pb (II) and Cd (II) from industrial effluent.

2. Materials and Methods

2.1. Sawdust Char preparation

The sawdust pod used for this study was collected within the Obafemi Awolowo University Ile-Ife, Osun State. Periwinkle shell was obtained from backyard dumpsites in Uyo, Akwa-Ibom State. Activated carbon (GAC F-300) by Boncaki Nigeria Limited Lagos, Nigeria was purchased commercially. The agricultural wastes were dried ground and sieved to particle size less than 300 μm . Less than 2 mm size fraction of periwinkle shell

and of the sawdust were used [20]. 100 g of the sieved sample was placed in a furnace (Carbolite RHF 1600) at 500 °C for 1h. The carbonaceous substance was allowed to cool to room temperature in an air tight crucible.

2.2. Activation of Sawdust Char

The charred samples were soaked in 2% H₂SO₄ (v/v) and placed in an oven at a temperature of 110°C for 24 h. The treated sample was washed with distilled water until the solution was not acidic. Then, the char was soaked in 2% NaHCO₃ (w/v) to remove the residual acid. The sample was finally dried in an oven at 110°C, cooled at room temperature and stored in a desiccator until use [21].

2.3. Characterization of the adsorbent

Scanning Electron Microscope (SEM) (High resolution SEM-Carl Zeiss) was used to study the surface morphological characteristics of the sawdust char. Rutherford backscattering spectrometry (RBS) (1.7 Mev Tandem Accelerator) was used to determine the elemental composition of the adsorbents [22, 23].

2.4. Chitosan Preparation

Periwinkle shell (50 g) after being washed, sun dried, ground and sieved to 2 mm particle size, was deproteinized with 4% (w/v) NaOH with constant stirring for 6 h at 80 °C. Thereafter, it was demineralized in 5% (v/v) HCl with constant stirring for 1 hour at room temperature. The sample was thoroughly washed until its acid free. The demineralized periwinkle particles was refluxed in acetone for 3 hours at 60°C to decolourize it. The content was filtered and dried, to get a snow white residue called chitin. The chitin was deacetylated in 50% (w/v) NaOH solution by constant stirring at 30 °C for 4 hours to produce chitosan.

2.5. Chitosan Gel Preparation

About 5 g of chitosan was slowly added to 100 ml of 10 % (w/v) oxalic acid with constant stirring. The mixture was also heated to 40-50 °C to facilitate mixing. A chitosan-oxalic acid mixture was formed (a whitish viscous gel).

2.6. Adsorbent Modification

The chitosan gel (100 ml) was diluted with water (~500 ml) and heated to 50 °C. 50 g of sawdust char was slowly added to the diluted gel, and mechanically agitated using a shaker (Flash Shaker SF1) operated at 200 osc/min for 24 h. The gel coated adsorbent were washed with distilled water, dried, and the soaked in 0.5 % (w/v) NaOH solution for 3 h. It was then extensively rinsed with distilled water and dried in an oven at 102 °C for 2 h, cooled at room temperature and stored in desiccator.

2.7. Batch Biosorption Studies

Batch adsorption studies were carried out using 1.0 g of the adsorbent and 50 ml of the Pb²⁺ and Cd²⁺ solutions with constant shaking using a shaker (Flash Shaker SF1) operated at 300 osc/min. The following parameters were investigated; Initial metal ion concentration (1, 2, 5, 10 and 20 mg/L), Biosorbent dose (0.5, 1.0, 1.5, 2.0 and 2.5 g), pH (3.5, 4.5, 5.5, 6.5 and 7.5) and Contact time (15, 30, 45, 60 and 90 min). The mixture was filtered using Whatman no.1 and the filtrate was analysed using atomic absorption spectroscopy (AAS).

The removal efficiency (E) of adsorbent on Cr (IV) are measured as follows:

$$\text{Adsorption Efficiency} = \frac{(C_0 - C_1)}{C_0} \times 100\% \quad (1)$$

Where:

C₀ is the initial concentration before adsorption

C₁ is the final concentration of metal solution (mg/L) in the filtrate after adsorption.

2.8. Data Evaluation

The amount of metal adsorbed by the adsorbent was calculated using a mass balance equation

$$Q = v (C_i - C_f)/m \quad (2)$$

where Q is the metal uptake (mg metal per g biosorbent), v is the liquid sample volume (ml), C_i is the initial concentration of the metal in the solution (mg/L), C_f is the final (equilibrium) concentration of the metal in the filtrate (mg/L) and m is the amount of the added biosorbent on the dry basis (g).

2.9. Adsorption Isotherm

Adsorption of metals from 50 ml of metal solution was carried out at different initial metal ion concentrations ranging from 1 to 25 mg/L; pH of 3.5 to 7.5, at 300 osc/min with the optimum agitation period of 60 min (optimum conditions of all pertinent factors was used) while maintaining the adsorbent dosage at 1.0 g. Langmuir and Freundlich models were applied to the adsorption isotherm and different constants were generated [24, 25].

The Langmuir model:

$$Q = Q_{\max} bC_f / 1 + bC_f \quad (3)$$

Where Q_{\max} is the maximum metal uptake under the given conditions, b a constant related to the affinity between the biosorbent and sorbate.

The linearized equation of Langmuir model is commonly represented by:

$$1/Q = 1/Q_{\max} (1/b C_f + 1) \quad (4)$$

The maximum metal uptake can be obtained if a plot of $1/Q$ against C_f is made. The second model is Freundlich model which mathematical equation can be written as in equation 3.

The Freundlich Model:

$$Q = k C_f (1/n) \quad (5)$$

Where k and n are Freundlich constant, which correlated to the maximum adsorption capacity and adsorption intensity, respectively.

Linearized Freundlich equation of equation 3 take the form (eqn 4)

$$\text{Log } Q = \text{Log } k + 1/n \text{ log } C_f. \quad (6)$$

A plot of $\text{log } Q$ against $\text{log } C_f$, will give a straight line which will confirm the Freundlich Isotherm.

3. Results and Discussion

3.1. Characterization of Adsorbent and Chitosan

Table 1 shows the elements present in the char of sawdust. The presence of other elements (O, Na, Mg, Al, Si, P, S, Cl, K, Ca, and Fe) aside carbon can enhance the adsorption through adsorption mechanism such as ion exchange, chelation, co-ordination and complexation reactions.

Scanning electron micrographs (SEM) as revealed in Figure 2 shows the morphological properties of the sawdust char. The typical irregular texture of the adsorbents reveals the adsorption sites which enhance adsorption.

Figure 3 shows the functional groups present in the chitosan extracted from periwinkle shell. The Fourier Transform Infra-Red (FTIR) analysis confirms the presence of **C—O** as shown by the stretching frequency at 1082 cm^{-1} . The 1492 cm^{-1} peak was due to the **CH₂** bonding stretching frequency and the band at 1467.54 cm^{-1} should be attributed to amine (**—NH₂**) of chitosan [26]. All peaks detected conforms with the functional groups of chitosan which confirms complete deacetylation of chitin to chitosan.

Table I: Elemental composition of Sawdust char

Element	Flamboyant pod	
	Weight%	Atomic%
C	42.87	56.19
O	34.37	33.82
Na	0.47	0.32
Mg	0.85	0.55
Al	1.2	0.70
Si	2.27	1.27
P	0.77	0.39
S	0.48	0.23
Cl	1.23	0.55
K	11.77	4.74

Ca	2.09	0.82
Fe	1.65	0.46

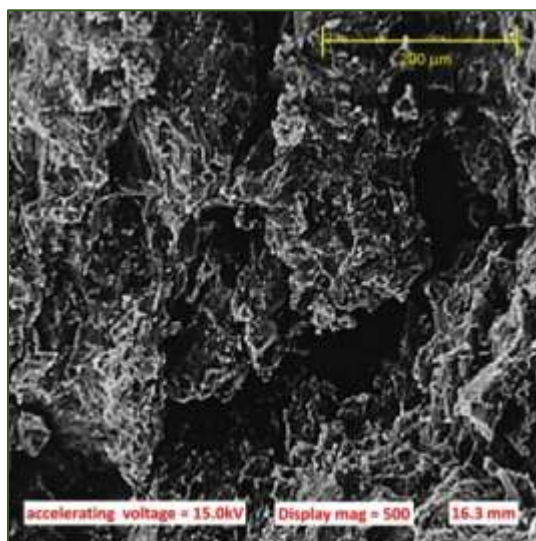


Fig. 2: Sawdust char SEM image

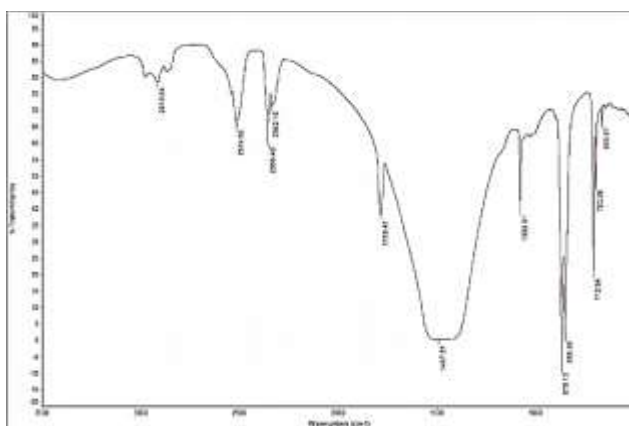


Fig. 3: FTIR of chitosan extracted from periwinkle shells

3.2. Effect of initial concentration on removal efficiency

Figure 4 shows the adsorption of Pb^{2+} by SC and MSC with varied initial concentration of metals, while other conditions were kept constant. Removal of Pb^{2+} by natural adsorbents (SC and MSC) and activated carbon was observed to be generally high. The removal efficiency increased with the initial concentration with best efficiency at 20 mg/l for Pb^{2+} . The efficiency of the modified adsorbent is observed to be higher than the unmodified adsorbent. The improved performance of MFPPC over FPPC is attributed to the presence of chitosan on MFPPC, the chitosan enhances the binding site available for metal uptake.

Figure 5 compares the adsorption efficiency of natural adsorbents (FPPC and MFPPC) with AC for the removal of Cd^{2+} from industrial effluent. The trend of Cd^{2+} removal is similar to that of Pb^{2+} but the removal efficiency of the former is generally lower compared to the later. The high adsorption of Pb^{2+} may be attributed to its higher selectivity. The order of metal selectivity is $Pb^{2+} > Cd^{2+}$.

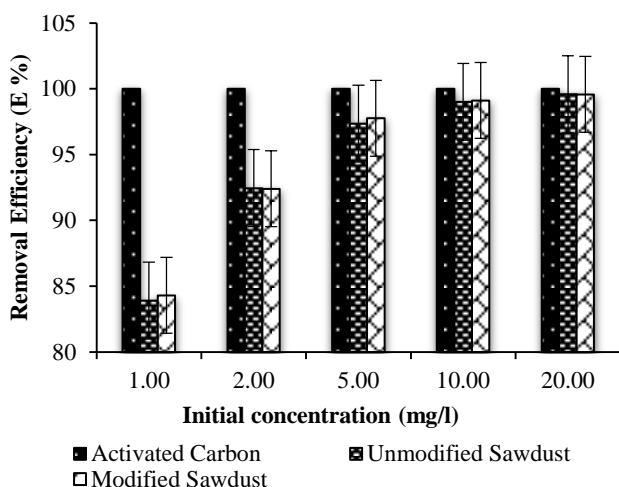


Fig. 4: Effect of initial concentration on Pb(II) removal [adsorbent dose = 1.0 g; contact time = 60 min; pH = 6.8; temp = 25°C]

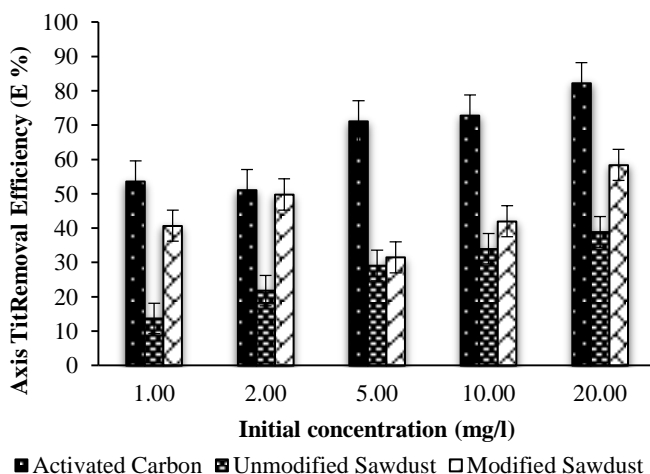


Fig 5: Effect of initial concentration on Cd(II) removal [adsorbent dose = 1.0 g; contact time = 60 min; pH = 6.8; temp = 25°C]

3.3. Effect of adsorbent dosage on adsorption

The effect of varying adsorbent dosage on the adsorption of Pb^{2+} and Cd^{2+} respectively are shown in Figure 7 and 8. Increase in adsorbent dosage has a corresponding effect on amount of metal removed from the aqueous solution with best efficiency at 2 g and 2.5 g adsorbent dosage respectively for Pb^{2+} and Cd^{2+} . The increase in metal uptake with increase in adsorbent dosage can be attributed to the availability of exchangeable sites as well as surface area in large quantities.

Chitosan modified sawdust char (MSC) demonstrate greater adsorption efficiency over the unmodified sawdust char (SC) while industrial activated carbon (AC) exhibits the highest removal efficiency even at small dosage (0.5 g). Modification of natural adsorbents with chitosan generally gives improved performance [4, 27, 28]. The trend of metal uptake by the adsorbents used is in the following order: activated carbon \geq modified adsorbents \geq unmodified adsorbents while the order of metal selectivity is $Pb^{2+} > Cd^{2+}$.

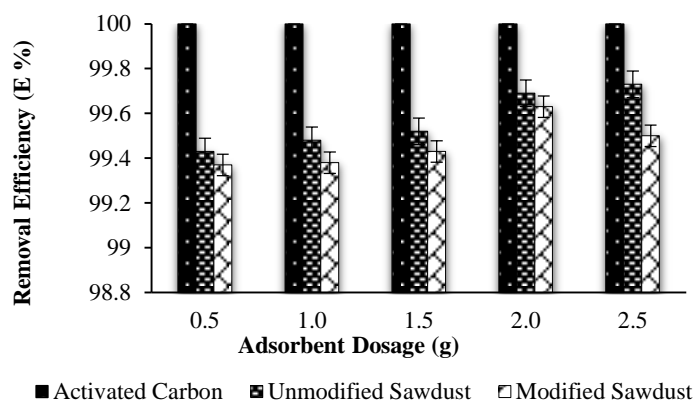


Fig 6: Effect of adsorbent dosage on Pb(II) removal [Pb(II) Conc. = 25 mg/L; adsorbent dose = 1.0 g; pH = 6.8; temp = 25°C]

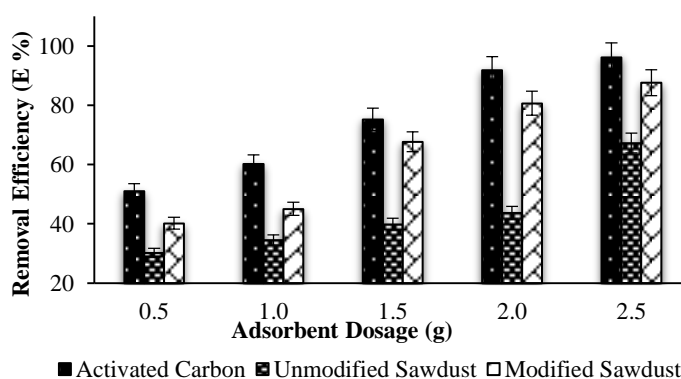


Fig. 7: Effect of adsorbent dosage on Cd(II) removal [Cd(II) Conc. = 25 mg/L; adsorbent dose = 1.0 g; pH = 6.8; temp = 25°C]

3.4. Effect of pH on Removal Efficiency

The pH of effluent is an important parameter for adsorption process, it influences adsorption capacity of the adsorbent. The pH of effluent used for this study was varied between 3.5 – 7.5 with a constant initial concentration of 20 mg/L, adsorbent dose of 1.5 g, and contact time of 60 min at 25 °C. Figure 5 and 6 respectively show the effects of pH on the uptake of Pb²⁺ and Cd²⁺ from aqueous solution. Adsorption efficiency of all adsorbents used increases with increase in pH with the best efficiency at pH 7.5 for both metals (Pb²⁺ and Cd²⁺). Adsorption is favoured at higher pH values (alkaline). Chitosan modified sawdust char exhibited a better adsorption capacity over unmodified sawdust char. Chitosan has good adsorptive characteristics which diminishes at low pH, this is due to its solubility at low pH, hence binding sites not readily available for sorption.

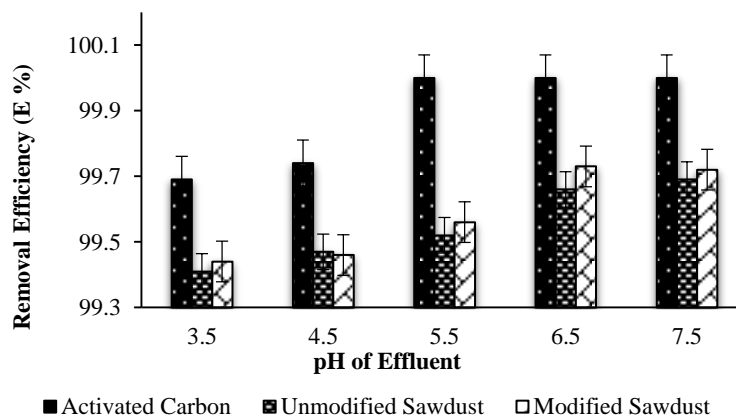


Fig. 8: Effect of pH on Pb(II) removal [Pb(II) Conc. = 25 mg/L; adsorbent dose = 1.0 g; contact time = 60 min; temp = 25°C]

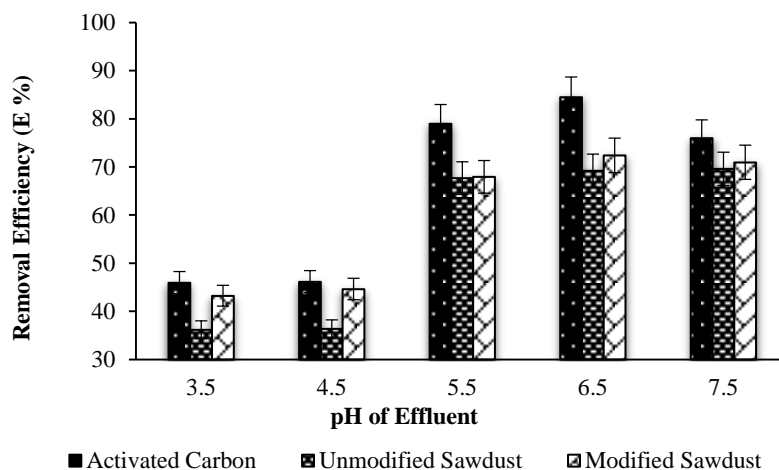


Fig 9: Effect of pH on Cd(II) removal [Cd(II) Conc. = 25 mg/L; adsorbent dose = 1.0 g; contact time = 60 min; temp = 25°C]

3.5. Effect of contact time on adsorption

The impact of contact time on metal uptake (Pb^{2+} and Cd^{2+}) by natural adsorbents (sawdust char and modified sawdust char) and industrial activated carbon was investigated with the aim of getting an optimum contact time for best adsorption result. Contact time was varied between 15 min and 90 min (15, 30, 45, 60 and 90 min). The impacts are presented in Figure 9 and 10 respectively for Pb^{2+} and Cd^{2+} .

Except for AC, metal uptake increased with contact time from 15 min and later stabilize from 60 min for both metals. This may be attributed to availability of vacant sites for adsorption in large quantity initially which later diminished due to the saturation of the vacant sites. Although AC exhibited the highest metal removal efficiency for both metals all through experimented contact time, natural adsorbents (SC and MSC) also show a substantial metal removal efficiency at contact time of 60 min and beyond.

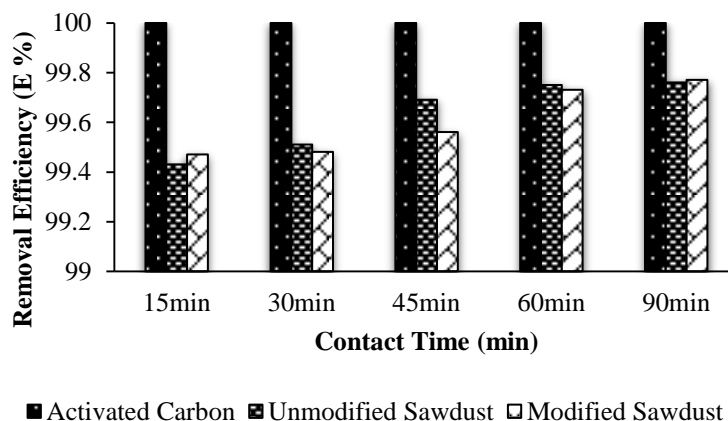


Fig. 10: Effect of contact time on Pb(II) removal [Pb(II) Conc. = 25 mg/L; adsorbent dose = 1.0 g; pH = 6.8; temp = 25°C]

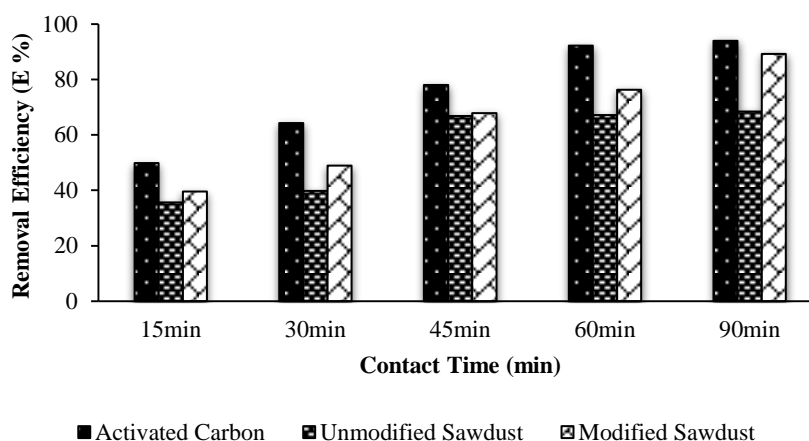


Fig.11: Effect of contact time on Cd(II) removal [Cd(II) Conc. = 25 mg/L; adsorbent dose = 1.0 g; pH = 6.8; temp = 25°C]

3.6. Adsorption Isotherm

Adsorption is usually described through an isotherm. The adsorption isotherm indicates how the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [29]. Adsorption capacity is usually predicted from equilibrium sorption isotherm [30].

Adsorption of metals from 50 ml of metal solution was carried out at different initial metal ion concentrations ranging from 1 to 25 mg/L; optimum conditions of all pertinent factors was used (pH of 6.8, agitation period of 60 min, adsorbent dosage of 1.0 g) while maintaining an oscillation of 300 osc/min. Langmuir and Freundlich models were applied to the adsorption isotherm and different constants were generated [24, 25].

The sorption performance of SC and MSC were assessed through the determination of adsorption isotherm with Pb^{2+} and Cd^{2+} for single metal sorption system as shown in Table 2 and 3 respectively. Langmuir isotherms constants (Q_{max} and b) are determined from the slope and intercepts of the plots of $1/Q$ against $1/C_f$, while the Freundlich isotherms constants (K and n) are obtained from the intercept and slope of the graph between $\log Q$ versus $\log C_f$.

The equilibrium experiment results show that Pb^{2+} and Cd^{2+} fitted well to the adsorption isotherms (Freundlich and Langmuir). The coefficient of correlation (R^2) for both model falls within $0 < R^2 < 1$ (Table 2 and 3). Freundlich isotherm exhibited a better fitting than Langmuir isotherm for Pb^{2+} by both SC and MSC with correlation coefficients of Freundlich isotherm (R^2_F) being higher than the correlation coefficients of Langmuir isotherm (R^2_L). The high correlation coefficient values (Table 2) of both Freundlich and Langmuir isotherms confirmed the suitability of these models [4, 27, 31]. In the case of adsorption of Cd^{2+} , Langmuir and Freundlich isotherms exhibit a trend for SC and MSC that is similar to adsorption of Pb^{2+} (Tables 3). Both Langmuir and Freundlich models fit better for Cd^{2+} than Pb^{2+} . The magnitude of the adsorption capacity (K) and adsorption intensity ($1/n$) obtained show the strong possibility for an easy separation of heavy metal ion from aqueous solution and a high adsorption capacity.

TABLE II: Langmuir and Freundlich constants for the adsorption of Pb^{2+} at 25°C

Adsorbent	Langmuir constants			Freundlich constants		
	b (L/mg)	Q_{max} (mg/g)	R^2_L	K	$1/n$	R^2_F
SC	-2.5471	4.9261	0.5975	8.3004	-0.2126	0.9348
MSC	-2.4098	4.6211	0.7239	7.9433	-0.2186	0.9440

R^2 = correlation coefficient.

TABLE III: Langmuir and Freundlich constants for the adsorption of Cd^{2+} at 25°C

Adsorbent	Langmuir constants			Freundlich constants		
	b (L/mg)	Q_{max} (mg/g)	R^2_L	K	$1/n$	R^2_F
SC	1.0345	333.3333	0.9526	147.3669	0.6618	0.9550
MSC	0.0580	1250.0000	0.9409	70.6643	0.8303	0.9015

R^2 = correlation coefficient.

4. Conclusion

This study showed that organic wastes such as sawdust and periwinkle shell could be processed to serve as an inexpensive, environment-friendly adsorbents to the commercially expensive activated carbon for treating heavy metal contaminated effluent. Best adsorption conditions observed for the natural adsorbents (sawdust char and modified sawdust char) are initial concentration of 20 mg/l for both metals; pH of 7.5 for both metals; adsorbent dosage of 2 g and 2.5 g respectively for Pb²⁺ and Cd²⁺; and contact time of 60 min for both metals. The uptake of Pb²⁺ by the natural adsorbents is observed to be higher than Cd²⁺ uptake, activated carbon exhibit the highest adsorption, but when modified with chitosan, the natural adsorbent exhibited a removal efficiency that is comparable with the industrial activated carbon. The results of adsorption isotherms illustrate that the adsorptive uptake of Pb²⁺ and Cd²⁺ by sawdust and modified sawdust chars could be described well with both Freundlich and Langmuir isotherms.

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