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Adsorption of Heavy Metals from Contaminated Water Using Sawdust as a Low Cost Adsorbent

FAROUQ A.U AND SAKPAIDE O.E
Department of Industrial Safety and Environmental Technology
Petroleum Training Institute
PMB 20, Effurun
Delta State
Nigeria

Abstract:
Background*: The presence of heavy metals like copper, cadmium and lead in water bodies due to the discharge of effluents is of great concern because of its toxic nature. Hence, there is great need to eliminate them to safe level before discharge. Sawdust, as an agricultural waste which is highly efficient, readily available and relatively inexpensive, has the potential to be an applicable alternative adsorbent for heavy metals.*
Materials and Methods*: Sawdust from a local furniture factory was procured. It was washed several times with distilled water to remove surface impurities and oven dried at a temperature of 75°C for 8 hours. The sawdust was then grinded to fairly fine particles and sieved to a mesh size of 40 mm. The dried and sieved material was stored in an airtight container for subsequent chemical treatment. In order to evaluate the efficiency of sawdust as a low cost adsorbent, to enhance the capacity of sawdust as the adsorbent, it was activated with sulfuric acid (H_2SO_4) and formaldehyde and eventually used as the adsorbent. The impact of adsorbent dosage, pH, and contact time was used as the controlling factors on the adsorption process.*
Results*: The results show that the optimum adsorption conditions of lead were at an adsorbent dosage of 10g (87.50%), pH of 5 (78.12%), and a contact time of 60 minutes (71.87%). For copper, optimum adsorption conditions was at an adsorbent dosage of 10g (52.94%), pH of 10 (55.29%), and a contact time of 60 minutes (47.64%). For cadmium, optimum adsorption conditions was at an adsorbent dosage of 10g (51.35%), pH of 10 (29.05%), and a contact time of 60 minutes (32.77%).*
Conclusion: *The result proves that low cost adsorbents, sawdust can be employed for the removal of Lead ions, Copper ions and Cadmium ions respectively.*
Key Word*: Heavy Metal, Adsorbent, Low-Cost, Sawdust.*

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I. Introduction

A low-cost adsorbent is any adsorbent that is naturally abundant or artificially available as a waste from industry and needs little or no processing[1]. Various researchers have employed the adsorption technique to remove heavy metals from waste streams, and activated carbon has been used extensively as an adsorbent. Activated carbon is still an expensive material, despite its widespread application in the water and wastewater treatment sectors. The necessity for safe and cost-effective technologies for removing heavy metals from contaminated waters has prompted research into the development of low-cost alternatives to commercially available activated carbon in recent years. As a result, it is critical that all potential sources of low-cost agro-based adsorbents be investigated and their suitability for heavy metal removal thoroughly assessed[2].

Heavy metal contamination is of the increase as a result of rapid industrialization and globalization in many parts of the word. In recent times, the extensive use of heavy metals has increased notably in industrial, domestic, agricultural, medical and technological applications. This has resulted to discharge of great amounts of metallic contaminated waste water and human exposure to these toxic elements has risen. Heavy metal water pollution presents a significant environmental problem requiring immediate intervention[3]. Heavy metals are persistent in nature and are a menance for both humans and the whole ecosystem due to their toxicity and mutagenic, immunogenic, carcinogenic and teratogenic action. The inherent persistent nature of heavy metals is a reason for concern as it bio-accumulates throughout the ecosystem and can be found at high levels in the soil, surface water, sediments and consequently reaching the food chain [4]. Heavy metal contamination is a severe environmental issue. Chemical precipitation, membrane filtration, oxidation, reverse osmosis, flotation, and adsorption are some of the methods that can be used to reduce the impact of harmful metal ions. However, due to the low concentration of metal uptake and economically viable properties, adsorption was found to be the most efficient and common among them. Cellulosic materials are low-cost and widely used, with a bright future ahead of them. These come in large quantities, are inexpensive, and have little or no economic worth. Fibers, leaves, roots, shells, barks, husks, stems, seeds, and other portions of cellulosic materials are employed as adsorbents[5].

Water pollution by harmful substances is a major source of worry for human health and environmental quality, and it has attracted a lot of scientific research. New and less expensive wastewater treatment systems are improving environmental quality and lowering negative consequences on fauna, flora, and humans. The sorption method is thought to be a cost-effective way to successfully remove heavy metals. There have been a growing number of studies in recent years dedicated to employing low-cost adsorbents such as bark, tannin-rich materials, lignin, chitosan peat moss, and sawdust[6].

Wood is a complicated substance that varies in heterogeneity depending on the tree type; it has a remarkable diversity and variability in its chemical composition. The composition of wood is gradually becoming a key subject of research for purposes of evaluation and practical application. The results of studies on several wood species revealed that they are mostly made up of cellulose (37-51%), hemicellulose (20-30%), lignin (20-30%), and extractives (20-30%). (1-5.5 percent) [7]. Sawdust has been widely reported lately for its ability of metal adsorption and removal from contaminated effluents. Consequently, scientists have ventured into studying different metals adsorption on varieties of sawdust. For instance [8], studied the efficiency of untreated beech sawdust for the removal of Cu(II) and Cr(III) from water solutions, which revealed a maximum adsorption ability of 30.22 mg.g-1 and 41.86 mg.g-1 for Cu(II) and Cr(III) respectively.

Adsorption has been discovered to be an intriguing approach for removing hazardous metals from waste water. It is now widely accepted as a reliable and cost-effective solution. It refers to the application of a solid material having adsorptive properties influenced primarily by its porous structure, surface area, and chemical structure[9]. This research was carried out to evaluate the adsorption capacity of sawdust as a low cost adsorbent in the adsorption of heavy metals from artificially contaminated water. The main objectives were the preparation and chemical activation of the sawdust; and determination of heavy metal concentration in the contaminated water after treatment with activated sawdust.

II. Material And Methods

Sample Preparation

Sawdust from a local furniture factory was procured. It was washed several times with distilled water to remove surface impurities and oven dried at a temperature of 75°C for 8 hours. The sawdust was then grinded to fairly fine particles and sieved to a mesh size of 40 mm. The dried and sieved material was stored in an airtight container for subsequent chemical treatment.

Absorbent Activation

100 gram of the dried sawdust was treated with 250ml 0f 0.2 N H_2SO_4

The sawdust was exposed to activation using sulfuric acid (H_2 SO_4).

Preparation of Adsorbent Solution

Three stock solutions were prepared by dissolving 1.5g of lead nitrate, cadmium carbonate and copper sulfate respectively in a beaker using distilled water. Thereafter, the solution was placed in 1 liter volumetric flask and made up to meniscus mark with distilled water to obtain a stock solution of 1000mg/L of metal ions. Several lower concentrations of 10ppm were prepared from the three stock solutions respectively by serial dilution.

Batch Adsorption Studies

In this study, batch adsorption experiments were performed at different conditions of time, temperature, time of interaction and adsorbent dosage. During each batch adsorption study, the concentration of lead, chromium and copper was determined using the Atomic Absorption Spectrometer.

Effect of Absorption Dosage

Batch experiments were performed using different masses (2g-10g) of adsorbent (activated sawdust) to investigate the influence of adsorbent dosage on the adsorption studies. The adsorbent of various dosages was added to 50ml of the aliquot solution of the lead ion, copper ion and cadmium ion solutions respectively and agitated with an orbital shaker at 200rpm for 30 minutes and eventually filtered. The heavy metal concentration of the filtrate was determined using the Atomic Absorption Spectrometer.

Effect of pH

Effect of pH (4, 5, 7, 9 and 10) was investigated to obtain the optimum pH condition. The pH of the solution was adjusted with 0.01M of sodium hydroxide and 0.01M hydrochloric acid. The solution was agitated with an orbital shaker at 200 rpm. The sample was filtered. The heavy metal concentration of the filtrate was determined using the Atomic Absorption Spectrometer.

Effect of Temperature

Batch absorption experiments were carried out to determine the influence of temperature on the adsorption study. Room temperature and a slightly elevated temperature of 31°C were used. 50ml of the aliquot solution of the lead ion, cadmium ion and copper ion was prepared. The sample was filtered. The heavy metal concentration of the filtrate was determined using the Atomic Absorption Spectrometer.

Effect of Contact Time

The effect of contact time on the rate of adsorption was studied varying the time from, 60, 120, 180 and 240 minutes to obtain the optimum contact absorption time. 50ml of the aliquot solution of the lead ion, cadmium ion and copper ion solution was prepared. The optimum pH, the adsorbent dosage and the optimum working temperature were all kept constant. The solution was agitated with an orbital shaker at 200 rpm. The sample was filtered out. The heavy metal concentration of the filtrate was determined using the Atomic Absorption Spectrometer.

Study Location: Petroleum Training Institute, Effurun.

Study Duration: September 2020 to September 2021.

III. Result

Efficiency of the Adsorbent for the Adsorption of Lead Ions

The formula, Efficiency $= \frac{CO - C1}{CO} \times 100$ was used to obtain the optimal adsorbent dosage, pH and contact time. Where C_O is the initial concentration and C_1 is the final concentration

Table no 1: Variation of adsorbent dosage for Lead

Dosage (g)	Initial concentration for lead (mg/l)	Final concentration for lead (mg/l)	Quantity of heavy metal extracted (mg/l)	Efficiency (%)
2	0.32	0.14	0.18	56.25
4	0.32	0.12	0.20	62.50
6	0.32	0.10	0.22	68.75
8	0.32	0.07	0.25	78.12
10	0.32	0..04	0.28	87.50

IV.

Table no 2: Variation of adsorbent dosage for Copper

Dosage (g)	Initial concentration for copper (mg/l)	Final concentration for copper (mg/l)	Quantity of heavy metal extracted (mg/l)	Efficiency (%)
2	1.70	1.20	0.50	29.41
4	1.70	1.09	0.61	35.88
6	1.70	0.95	0.75	44.11
8	1.70	0.89	0.81	47.64
10	1.70	0.80	0.90	52.94

V.

Table no 3: Variation of Adsorbent Dosage for Cadmium

Dosage (g)	Initial concentration for cadmium (mg/l)	Final concentration for cadmium (mg/l)	Quantity of heavy metals extracted (mg/l)	Efficiency (%)
2	2.96	1.97	0.99	33.44
4	2.96	1.89	1.07	36.14
6	2.96	1.73	1.23	41.55
8	2.96	1.52	1.44	48.64
10	2.96	1.44	1.52	51.35

Table 1, 2 and 3 show the variation of adsorbent dosage for the adsorption studies highlighting the initial concentration, final concentration, quantity of heavy metals extracted and efficiency of Lead, Copper and Cadmium respectively. From table no 1, 10g (87.50%) of the adsorbent (activated sawdust) extracted more of lead ions while 2g (56.25%) of the adsorbent extracted the least lead ions. In table 2, 10g (52.94%) of the adsorbent adsorbed more of the copper ions while the least lead ions were absorbed by the adsorbent dosage of 2g (29.41%). From table 3, 10g (51.35%) of the adsorbent extracted more cadmium ions while the least was absorbed by 2g (33.44%) of the adsorbent. Table 4 is the summary of table 1, 2 and 3. It compares the different efficiencies of the adsorbent for the adsorption studies of lead, Copper and Cadmium respectively.

Table 4: Efficiencies for Removal of Lead, Copper and Cadmium versus Dosage

Dosage (g)	Efficiency for Lead (%)	Efficiency for Cadmium (%)	Efficiency for Copper (%)
2	56.26	33.44	29.14
4	62.50	36.14	35.88
6	68.75	41.55	44.11
8	78.12	48.64	47.64
10	87.50	51.35	52.94

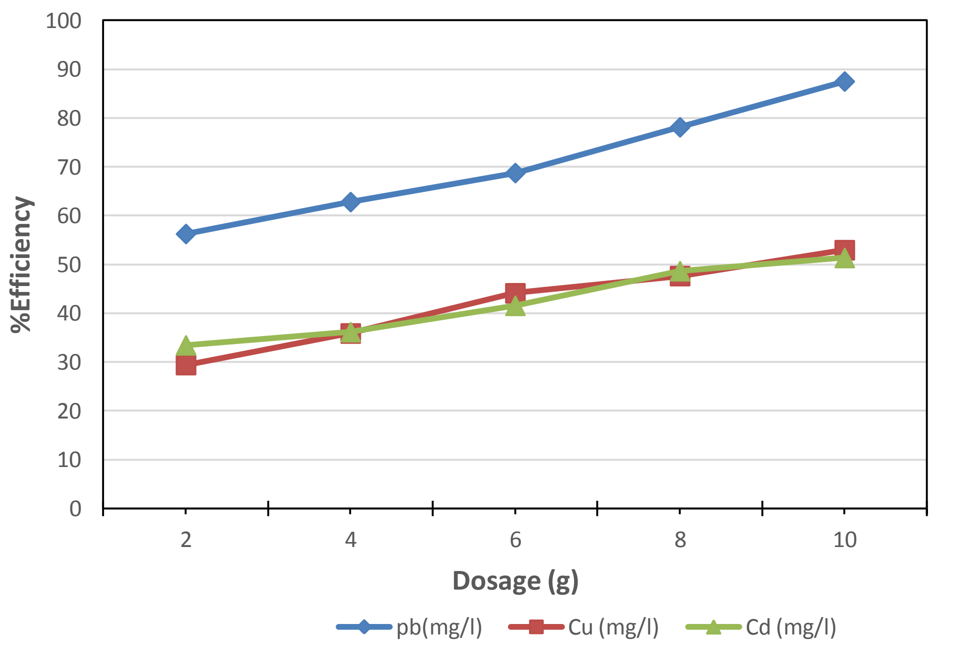

Figure1: Efficiency of Adsorption Against Dosage

Table no 5: Variation of pH for Lead

pH	Initial concentration for lead (mg/l)	Final concentration for lead (mg/l)	Quantity of metal extracted (mg/l)	Efficiency (100%)
4	0.32	0.11	0.21	65.62
5	0.32	0.07	0.25	78.12
7	0.32	0.09	0.23	71.87
9	0.32	0.13	0.19	59.37
10	0.32	0.16	0.31	50.00

Table no 6: Variation of pH for Copper

pH	Initial concentration for copper (mg/l)	Final concentration for copper (mg/l)	Quantity of heavy metals extracted	Efficiency (100%)
4	1.70	0.95	0.75	44.11
5	1.70	0.90	0.80	47.05
7	1.70	0.92	0.78	45.88
9	1.70	0.79	0.91	53.25
10	1.70	0.76	0.94	55.29

Table no 7: Variation of pH for Cadmium

pH	Initial concentration for Cadmium (mg/l)	Final concentration for Cadmium (mg/l)	Quantity of heavy metals Extracted	Efficiency (100%)
4	2.96	2.29	0.67	22.63
5	2.96	2..21	0.75	25.33

7	2.96	2.33	0.63	21.28
9	2.96	2..19	0.77	26.01
10	2.96	2.10	0.86	29.05

Table no 8: Efficiencies for Removal of Lead, Copper and Cadmium against pH

	pH				
	2	**5**	**7**	**9**	**10**
Efficiency for Lead	65.62	78.12	71.87	59.37	50.00
Efficiency for Cadmium	22.63	25.33	21.28	26.01	29.05
Efficiency for Copper	44.11	47.05	45.88	53.25	55.29

Table 5, 6 and 7 revealed the variations of pH for the adsorption studies highlighting the initial concentration, final concentration, quantity of heavy metals extracted and efficiency of lead, copper and cadmium respectively. From table 5, of the adsorbent (activated sawdust) extracted more of lead ions at a pH of 5 (78.12%) while the least was at a pH of 10 (50.00%). In table 6, the highest amount of copper removed was at a pH of 9 (53.25%) while the least adsorbed was at a pH of 4 (44.1%). From table 7, the highest amount of cadmium was at a pH of 10 (29.05%) while the least adsorbed was at a pH of 7 (21.28%). Table 8 is the summary of table 5, 6 and 7, which compares the different efficiencies of the adsorbent for the adsorption studies of Lead, Copper and Cadmium respectively.

Table no 9: Contact Time Variation for Lead

Contact time (min)	Initial concentration for Lead (mg/l)	Final concentration for Lead (mg/l)	Quantity of heavy metals extracted (mg/l)	Efficiency (100%)
15	0.32	0.15	0.17	53.13
30	0.32	0.11	0.21	65.63
60	0.32	0.09	0.23	71.88
120	0.32	0.19	0.13	40.63
240	0.32	0.20	0.12	37.50

Table no 10: Contact Time Variation for Copper

Contact Time (min)	Initial Concentration for Copper (mg/l)	Final Concentration for Copper (mg/l)	Quantity of Heavy Metals Extracted	Efficiency (100%)
15	1.70	1.27	0.43	25.29
30	1.70	0.93	0.77	45.29
60	1.70	0.89	0.81	47.65
120	1.70	1.32	0.38	22.35
240	1.70	1.37	0.33	19.41

Table no 11: Contact Time Variation for Cadmium

Contact Time (mins)	Initial of Concentration of Cadmium (mg/l)	Final Concentration of Cadmium (mg/l)	Quantity of Metal Extracted (mg/l)	Efficiency (100%)
15	2.96	2.12	0.84	28.38
30	2.96	2.09	0.87	29.39
60	2.96	1.99	0.97	32.77
120	2.96	2.29	0.67	22.64
240	2.96	2.30	0.66	22.30

Table no 12: Efficiencies for Removal of Lead, Copper and Cadmium against Contact Time

Contact Time (mins)	Efficiency (%) for Lead	Efficiency (%) For Copper	Efficiency (%) For Cadmium
15	53.13	25.29	28.38
30	65.63	45.29	29.39
60	71.88	47.65	32.77
120	40.63	22.35	22.64
240	37.50	19.41	22.30

Table 12 is the summary of table 9, 10 and 11. It shows the most favorable contact time (60 minutes) and the least optimal contact time (240 minutes) for the adsorption studies of lead, copper and cadmium respectively. As the contact time increased, the efficiency also increased.

IV. Discussion of Results

The efficiency of sawdust as a low cost adsorbent has been studied for the extraction of lead, copper and cadmium. Batch experiments were carried out in all interactions using 50 ml of Lead nitrate; Copper Sulfate and Cadmium Carbonate solutions and agitated with an orbital shaker with a constant speed of 200 rpm for 20 minutes

Effect of Adsorbent Dosage

From figure 1, it can be observed that as the adsorbent dosage increases, the adsorption capacity of the adsorbent increases for Lead, Copper and Cadmium respectively. The increase in adsorbent dosage with increasing adsorbent dosage arises because of the increased availability of exchange sites or surface areas at high concentrations of adsorbents. The effect of adsorbent dosage on the adsorption of metals showed that the percentage of metal removed increased with increase in adsorbent dosage due to increased adsorption surface area [2]. Similar trend has been observed in other studies. In the work carried out by [10], on the adsorption of Cu and Ba from aqueous solutions using nano particles of *origanum (OR)* and *lavandula (LV),* 0.1 -2g of the adsorbent was used for the adsorption of Copper and Barium. It was observed as the adsorbent dosage increases, the greater the rate of removal.

Effect of pH

The effect of pH on the adsorption process was tabulated in table 8. The maximum uptake of Lead occurred at pH of 5 (78.12%), which corroborate the findings of [11] where they reported that optimum pH for the adsorption of copper (II) and lead (II) ions was found to be 4.0 and 5.0 respectively.

From table 6, it can be clearly seen that for the adsorption of copper ions, an increase in pH leads to an increase in the rate of removal of copper ions. A similar observation is seen in the work “Adsorption of Copper ions From Aqueous Solutions Using Low Cost Adsorbent’ carried out by [12]. The reason for this is that, at lower pH values, the surface sites on the adsorbents is positive and adsorption was not favorable but higher pH values results to electro static repulsion between cations and the surface sites, thereby the competing effects of the H^+ ions decreases and the positively charged Cu (ii) ions get adsorbed on the free binding sites, resulting to an increase in the total metal uptake. In this study, the optimal pH for copper adsorption was at a pH of 10 (78.12%) while the least was at a pH of 4 (44.11%).

The pH is one of the most important factors affecting adsorption. Table 8 shows the experimental result. With an increase in pH, there is a greater removal of cadmium ions between the pH of 4 and 5. At the pH of 7, there was a decrease in the % rate removal but beyond this point, the adsorption rate for the removal of cadmium increased making the optimal pH for the adsorption of cadmium to be 10. Quite similar observations were seen in the work carried out by [13]. In their work titled ‘the adsorption of cadmium and lead ions from the synthesis of wastewater with activated carbon: optimization of single and binary terms, as the pH increases, the rate of removal of cadmium also increases with maximum removal at a pH of 7-8. For cadmium, the efficiency at a pH of 4, 5, 7 9 and 10 is 22.63%, 25.33%, 21.28%, 26.01% and 29.05% respectively. The optimal pH for cadmium adsorption was at a pH of 10 (29.05%) while the least was at a pH of 7 (21.28%)

Effect of Contact Time

In order to determine the influence of contact time on the adsorption studies, a time interval of 15 minutes, 30 minutes, 60 minutes, 120 minutes and 240 minutes was used.

From table 12, the rate of removal of Lead ions, Copper ions and Cadmium ions increases with an increase in contact time. However, after the contact time of 60 minutes, there was a decrease in the adsorption capacity of the adsorbent. This is as a result of the decrease in the available active sites (exchange sites). Similar observations were reported by [14], in their work titled ‘competitive effects for the adsorption of Copper, Cadmium and Lead ions using modified activated carbon from bamboo’. A dosage amount of 0.02g, 0.04g and 0.06g had an efficiency of 89.0%, 97.4% and 99.5% respectively.

The same trend was seen in the adsorption of Copper ions. The optimal contact time for the adsorption of Copper ions was 60 minutes. As the contact time increases, the adsorptions capacity of the adsorbent also increases. However, this trend of increase was not completely exponential. Maximum removal occurred at 60 minutes. And then there was a decrease in the adsorption capacity of the adsorbent. The reason for this decrease could be active sites been completely exhausted. This same trend was seen in the adsorption of cadmium ions. The contact time of 15 minutes, 30 minutes, 60 minutes, 120 minutes and 240 minutes yielded an efficiency removal of 28.37%, 29.39%, 32.77%, 22.63% and 20.94% respectively. The maximum removal was at the contact time of 60 minutes. After that time there was also a reduction in the adsorption capacity of the adsorbent for lead and cadmium. This also, could be due to the available exchange sites been completely exhausted.

V. Conclusion

Expensive adsorbents can be replaced by low cost adsorbents such as sawdust. In this study the adsorption of copper, cadmium and lead was investigated with respect to contact time, pH and adsorbent dosage. The adsorption experiments showed that activated sawdust is suitable and effective for the removal of heavy metals from simulated acidic and alkaline solutions and also provides promising perspective for use in purification of metals from wastewaters.

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