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Bioabsorption of Maize Cob and its Derivative in the Elimination of Heavy Metals from Waste Water in Some Local Government Areas of Kaduna State, Nigeria

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Abstract

Industrial waste water is a significant cause of water pollution. Many health challenges can be linked to high intake of heavy metals directly or indirectly into the body system beyond which is required to function adequately. This study evaluated the bioabsorption potentials of Maize Cob (MC), Maize Cob Charcoal (MCC), and Ethylenediamine-disuccinate treated Maize Cob (ETMC) in the elimination of heavy metals from industrial waste water in Kaduna South and Chikun Local Government Areas. Industrial waste water samples were collected from Defence Industries Corporation of Nigeria (DICON), Bam Paint Industry (BAM-PAINT), Chellco Industry (CHELLCO) and Nigerian Breweries plc (NBC). Heavy metals were analyzed using Atomic Absorption Spectrophotometry (AAS). MC, MCC and ETMC were used to treat the industrial waste water through Batch sorption experiment at 0.42mm particle size. Zinc (Zn^{2+}), Copper (Cu^{2+}), Cadmium (Cd^{2+}), Nickel (Ni^{2+}) and Lead (Pb^{2+}) were the detected at different concentrations across the samples. The results showed that concentration of Zn^{2+} ion present in the study areas ranged from 0.442 ± 0.005 to 3.943 ± 0.031mg/g. Cu^{2+} ion ranged from 0.226 ± 0.003 to 9.730 ± 0.001 mg/g, Cd^{2+} (-0.040± 0.005 to 0.624 ± 0.003 mg/g), Ni^{2+} (0.184 ± 0.004 to 12.096 ± 0.003 mg/g) and Pb^{2+} (-0.142± 0.003 to 1.128 ± 0.002 mg/g). Heavy metal absorption efficiencies by MC differ significantly ($p < 0.05$). MC had the highest adsorption rate (92%) for Zn^{2+} ion in DICON Company waste water. Cu^{2+} was reduced by 40% in waste water from BAM-PAINT Company, 94% for Cd^{2+} ion in NBC waste water, 72% for Ni^{2+} and 98% of Pb^{2+} in NBC waste water. Heavy metal removal efficiency after using MCC showed significant difference ($p < 0.05$) in the heavy metals adsorption rate. There was 85% reduction in the concentration of Zn^{2+} and 40% of Ni^{2+} in industrial waste water from DICON Company. The absorbent was most effective in reducing the concentration of Cu^{2+} ion present in NBC by 187% and 154% of Cd^{2+} ion in sample from BAM-

PAINT Company, while, Ni^{2+} and Pb^{2+} had reduction rate of 60% and 95% at DICON and NBC respectively. ETMC drastically reduced the concentration of Zn^{2+} ions from to -604.533 ± 2.512 mg/g in CHELLCO industry and Cu^{2+}ions to -9.567 ± 0.351 mg/g in BAM-PAINT waste water. Therefore, it can be concluded that Maize Cob, Maize Cob Charcoal and Ethylene diamine disuccinic treated maize cob are effective absorbent for eliminating lead, zinc, cadmium, nickel and copper from waste water.

Keywords: Bioabsorption; Heavy metal; Industry; Waste water; Pollution; Elimination.

1. Introduction

The increasing use of potentially toxic elements in recent decades has inevitably led to a surge of metallic and other harmful substances in both aquatic and terrestrial environments [1, 2]. A significant contributor to this pollution is the discharge of untreated wastewater into the environment. Wastewater, which can come from domestic, industrial, commercial, or agricultural activities, varies in composition based on its source [3]. Many industries produce and utilize numerous synthetic substances, many of which are non-biodegradable or decompose very slowly. These persistent substances remain in the environment for long periods, gradually becoming more concentrated [4]. They accumulate in living tissues throughout the food chain, posing serious threats to human and public health [5].

Various methods have been employed to treat wastewater and mitigate the release of toxic substances, including oxidation [6], coagulation [7], solvent extraction [8], ion exchange [9], membrane separation [10], and reverse osmosis [11]. However, these methods are often not economically viable for small and medium-sized industries due to their high operational and maintenance costs, the generation of toxic sludge, and the complexity of the procedures involved. An emerging solution is the use of biosorbents for removing toxic pollutants or recovering valuable resources from aqueous wastewater (biosorption or adsorption), representing a recent development in environmental and bio-resource technology [4]. The main advantages of biosorption over conventional methods include lower costs, higher efficiency, reduced chemical and biological sludge, no need for additional nutrients, the ability to regenerate biosorbents, and the possibility of metal recovery after adsorption [12-14]. Biosorbents have demonstrated effectiveness in treating wastewater pollutants, achieving up to 90% adsorption of pollutants [4].

Common biosorbents used in the biosorption process include activated carbon [11], clay [13], kaolin [14], carbon nanotubes [4], metal nanoparticles [1], nanocomposites [12], functionalized carbonaceous materials, agricultural wastes [15], goethite, modified cellulose, and native cassava starch hydrogel [15]. These materials have emerged as cost-effective and efficient alternatives for wastewater treatment in the past two decades. A variety of agricultural wastes and by-products have been studied for their ability to remove pollutants from wastewater [16]. Effective biosorption using agricultural waste involves the carbonization and activation of these materials. Carbonization involves the thermal decomposition of raw materials, removing non-carbon species and creating a fixed mass with a basic pore structure [17]. Activated carbon, an odorless and tasteless powder, can absorb large amounts of chemicals or poisons [18, 19].

Maize, also known as corn, is a cereal grass grown for food or livestock fodder [20]. In Nigeria, maize is a staple agricultural product grown in almost all parts of the country, serving as a major ingredient in various foods and consumed directly when boiled or roasted. The maize cob, a natural waste product from maize, can cause significant environmental pollution if not properly managed. After harvesting maize grain, the cobs, produced in large quantities, have minimal use and are often left in piles in homesteads and fields. This abundance makes maize cobs readily available for use as activated carbon. The ratio of maize grain to cob is approximately 100:18 [21]. Without proper utilization, this can lead to the useless accumulation of maize cobs, especially in Nigeria [21].

Research indicates that chemical treatment with chelating agents and thermal modification can enhance the sorption capacity of maize cobs. Consequently, modifying maize cobs with EDDS (Ethylene-Diamine-Disuccinate) can improve their ability to eliminate heavy metals. EDDS is a suitable alternative to EDTA because it is readily biodegradable and less toxic to fish and fungi [22]. Kaduna State, Nigeria, is home to many poorly regulated metal recycling factories, mechanic workshops, and similar operations that release their effluents directly into the environment. This study therefore, investigated the biosorption potential of maize cob and its derivatives for removing heavy metals from wastewater in Kaduna South and Chikun Local Government Areas of Kaduna State, Nigeria.

2. Materials and Method

2.1 Sample Collection

Maize cobs (Figure 1A) were obtained from a local farm in Agwa, Kudenda extention, chikun Local Government Area of Kaduna State. These were ground into powder form (Figure 1B), then oven dried at 50°C for 72 hours. The meal obtained was sieved using 0.42 mm and 0.78 mm mesh respectively. After which it was rinsed with deionized water and air dried then stored for use as described by Igwegbe, *et al.* [23].

2.2. Preparation of Maize Cob Charcoal

The corn cobs were washed with distilled water and allowed to air dry. Distilled water was used to wash the maize cobs. The dry maize cob was burned to a temperature of 400°C for 15 minutes without any air in the furnace before being sun-dried. The resulting charcoal (Figure 1C) was allowed to cool in air and crushed to smaller particles using pestle and mortar.

2.3. Preparation of Ethylene Diamine Disuccinic Acid (EDDS) Treated Maize Cob

One thousand seven hundred and fifty (1750) ml of water and 200g of maize cob was added respectively to 5 beakers. Ten grams of EDDS was added to each of the beakers. It was stirred and boiled for 1 hour with heating by electric cooker. The mixture was placed at ambient temperature for 8 hours. Thereafter, it was rinsed copiously with deionized water, filtered and dried at 105^{o}C. This was used as the EDDS modified absorbent (Figure 1D) for analysis as reported.

2.4. Carbonization and Ashing of Maize Cob and its Derivatives

Figures 1A - D show photos of surfaces of Unprocessed Maize Cob, Maize Cob Powder, Maize Cob Charcoal Powder, and Maize Cob Powder Treated with EDDS.

Figure 1A Unprocessed Maize Cob

Figure 1B Maize Cob Powder

Figure 1C Maize Cob Charcoal Powder

Figure 1D EDDS Treated Maize Cob Powder

2.5. Waste Water Analysis

Wastewater was collected from four industries: Defence Industries Corporation of Nigeria (DICON), Bam Paint Industry (BAM-PAINT), Chellco Industry (CHELLCO), and Nigerian Breweries plc (NBC) located in Kaduna South and Chikun LGA of Kaduna State. The samples were labeled A-D. These wastewater samples were transported to the laboratory for heavy metal content analysis. For the analysis, 50 ml of each sample was placed in a 100 ml beaker and mixed with 10 ml of concentrated nitric acid. The mixture was digested in a fume hood until a colorless gas was emitted, indicating the end of the digestion process. After cooling, the digest was rinsed with distilled water, filtered, and transferred to a 100 ml volumetric flask, where it was diluted to the mark with distilled water. The presence of heavy metals was then determined using an atomic absorption spectrometer (AAS).

2.4. Sorption Experiment

The adsorption experiment was carried out in a 250 cm³ conical flask covered with aluminum foil. A measured amount (0.2 g) of unmodified maize cob (adsorbent) was added to 100 cm³ of the wastewater sample. The mixture was shaken for an hour using a Stuart flask shaker. After the contact time, the reaction mixture was filtered through Whatman filter paper, and the metal ions in the filtrate were identified using an atomic absorption spectrophotometer. The difference between the initial and final concentrations of metal ions in the solutions was used to calculate the amount of metal absorbed by the maize cob. The process was repeated for maize cob charcoal and Ethylene-diamine-disuccinate Treated Maize Cob. The adsorption capacity and percentage removal were calculated using the following equations:

$$Q = (Co - Ce) \qquad 1$$

$$\%R = \frac{Co - Ce}{Co} X\,100 \qquad 2$$

Where Q is the adsorption capacity of the adsorbent, %R represents the percentage removal, Co is the concentration of the metal ions before adsorption, and Ce is the concentration of the metal ions after adsorption.

3. Results

Table 1 presents the concentrations of heavy metals in industrial wastewater before the sorption reaction. The detected heavy metals in the study areas include Zinc (Zn^{2+}), Copper (Cu^{2+}), Cadmium (Cd^{2+}), Nickel (Ni^{2+}), and Lead (Pb^{2+}). The results indicate significant differences ($P \geq .05$) in the mean concentrations of Zn^{2+}, Cu^{2+}, Cd^{2+}, $Ni^{2+}$and Pb^{2+} across the study sites. The mean concentration of Zn^{2+} was significantly higher in CHELLCO (3.943 ± 0.031 mg/g) and lowest in NBC (0.442 ± 0.005 mg/g). The highest mean concentration of Cu^{2+} was observed in DICON (9.730± 0.001 mg/g) but was significantly low in CHELLCO and NBC (0.226 ± 0.003 mg/g). There was no difference in the mean concentration of Cd^{2+} in all study areas except for BAM PAINT (0.624 ± 0.003 mg/g). The mean concentrations of Ni^{2+} (12.096 ± 0.003 mg/g) and Pb^{2+} (1.128 ± 0.002 mg/g) were significantly higher in DICON and BAM PAINT, respectively.

Table-1. Heavy Metal Concentration (mg/g) in Industrial Waste Water before Sorption Reaction

Metals	BAM PAINT (mg/g) Mean + S.D	CHELLCO(mg/g) Mean + S.D	DICON (mg/g) Mean + S.D	NBC (mg/g) Mean + S.D
Zinc	1.473 ± 0.003^b	3.943 ± 0.031^c	1.578 ± 0.003^b	0.442 ± 0.005^a
Copper	1.257 ± 0.002^b	0.226 ± 0.003^a	9.730± 0.001^c	0.226 ± 0.003^a
Cadmium	0.624 ± 0.003^b	-0.040± 0.005^a	0.133± 0.152^a	0.037 ± 0.002^a
Nickel	0.633 ± 0.002^a	0.184 ± 0.004^a	12.096 ± 0.003^b	0.187 ± 0.002^a
Lead	1.128 ± 0.002^b	-0.142± 0.003^a	-0.143± 0.003^a	0.232 ± 0.004^a

Results are presented as Mean ± SD. Values with different superscript alphabets across the rows are significantly different from each other at $P \leq 0.05$. Post-Hoc Test (Tukey), n=3.

Table 2 presents the efficiency of heavy metal removal from industrial wastewater after sorption using Maize Cob (MC). The removal efficiencies by Maize Cob (MC) varied significantly ($p < 0.05$). The results showed that 92% of Zn^{2+} was absorbed in DICON wastewater, which is comparable to the absorption rate of Cu^{2+} (76.5%). The wastewater sample from NBC exhibited the highest removal rates for Cd^{2+} (93.6%), Ni^{2+} (72.3%), and Pb^{2+} (98%).

Table-2. Effect of Maize Cob on Percentage Removal of Heavy Metal Ions (0.42mm)

Metals	BAM PAINT (%) Mean + S.D	CHELLCO (%) Mean + S.D	DICON (%) Mean + S.D	NBC (%) Mean + S.D
Zinc	-59.267± 1.429^a	-5.200 ± 0.100^a	92.200 ± 0.954^b	-25.533 ± 1.0600^a
Copper	40.733 ± 0.586^a	188.533 ± 0.153^c	76.500 ± 0.819^b	223.800 ± 2.265^d
Cadmium	27.367 ± 0.208^a	86.733± 0.153^b	85.333 ± 1.102^b	93.567 ± 0.611^c
Nickel	-8.400 ± 0.436^a	-60.500 ± 0.608^a	45.833 ± 0.551^b	72.300 ± 1.277^c
Lead	-139.767 ± 0.153^a	-52.233± 0.643^a	-22.433 ± 0.702^a	98.033 ± 1.201^b

Results are presented as mean ± SD. Values with different superscript alphabets across the rows are significantly different from each other at $P \leq 0.05$. Post-Hoc Test (Tukey), n = 3.

Table 3 shows the heavy metal removal efficiency from industrial wastewater after sorption using Maize Cob Charcoal (MCC) with a 0.42mm particle size. There were significant differences ($p < 0.05$) in the removal efficiency of heavy metals by MCC. In DICON Company, 85% of Zn^{2+} and 60.6% of Ni^{2+} were removed. The absorbent was most effective in reducing the concentration of Cu^{2+} ion present in NBC by 187%. Cd^{2+} ion was also drastically reduced by 154% in the sample from BAM-PAINT Company. The highest adsorption of Ni^{2+} (60%) occurred in the wastewater sample from DICON Company. The sample from NBC showed a high removal rate of Pb^{2+} (95%).

Table-3. Effect of Maize Cob Charcoal (MCC) on Removal of Heavy Metal Ions

Metals	BAM PAINT (%) Mean ± S.D	CHELLCO (%) Mean ± S.D	DICON (%) Mean ± S.D	NBC (%) Mean ± S.D
Zinc	-66.067± 0.306[a]	58.500 ± 0.458[b]	85.200 ± 1.300[c]	-36.133 ± 3.386[a]
Copper	40.000 ± 0.361[a]	134.467 ± 2.159[c]	81.567 ± 2.775[b]	186.533 ± 1.528[d]
Cadmium	154.900 ± 0.625[d]	92.733 ± 1.474[b]	97.833 ± 1.582[c]	42.533 ± 1.528[a]
Nickel	40.400 ± 1.015[a]	-3.3667 ± 0.681[a]	60.560 ± 0.589[a]	-503.633 ± 2.113[a]
Lead	-11.367 ± 1.474[b]	-68.767 ± 2.0033[a]	-44.467 ± 1.626[c]	94.767 ± 0.850[b]

Results are presented as Mean ± SD. Values with different superscript alphabets across the rows are significantly different from each other at $P \leq 0.05$. Post-Hoc Test (Tukey), n = 3.

Table 4 presents the heavy metal sorption efficiency by Ethylene Diamine Disuccinate treated Maize Cob (ETMC) with a 0.42mm pore size. The results showed a significant ($P < 0.05$) reduction in the concentrations of Zn^{2+}, Cu^{2+}, Cd2+, Ni^{2+}, and Pb^{2+} in industrial wastewater from different study areas. ETMC drastically reduced the concentration of Zn^{2+} ions from 3.943 ± 0.031 to -604.533 ± 2.512 mg/g in CHELLCO industry and from 0.442 ± 0.005 to -4.777 ± 2.000 mg/g in NBC industrial wastewater. Cu^{2+} ions in BAM-PAINT wastewater were reduced from 1.257 ± 0.002 to -9.567 ± 0.351 mg/g and from 9.730 ± 0.001 to -4.777 ± 0.179 mg/g in DICON wastewater. Ni2+ was reduced from 0.633 ± 0.002 to -794.033 ± 1.815 mg/g in BAM-PAINT wastewater and from 12.096 ± 0.003 to -22.233 ± 1.528 mg/g in DICON wastewater. Pb^{2+} ion concentration was also adsorbed from 1.128 ± 0.002 to -1095.933 ± 3.219 mg/g, from -0.142 ± 0.003 to -2054.800 ± 6.245 mg/g, and from -0.143 ± 0.003 to -933.900 ± 2.000 mg/g for BAM-PAINT, CHELLCO, and DICON wastewater, respectively.

Table-4. Effect of Ethylene Diamine Disuccinate treated Maize Cob (ETMC) on Heavy Metal Ions Removal

Metals	BAM PAINT(mg/g) Mean ± S.D	CHELLCO(mg/g) Mean ± S.D	DICON (mg/g) Mean ± S.D	NBC (mg/g) Mean ± S.D
Zinc	147.100 ± 1.609[b]	-604.533 ± 2.512[a]	222.400 ± 771.802[c]	-4.777 ± 2.000[a]
Copper	-9.567 ± 0.351[a]	1111.933 ± 1.528[c]	-4.777 ± 0.179[a]	524.167 ± 2.517[b]
Cadmium	3336.033 ± 2.859[b]	15648.600 ± 2.000[c]	3514.300 ± 2.000[b]	25.000 ± 1.000[a]
Nickel	-794.033 ± 1.815[a]	6583.267 ± 2.082[b]	-22.233 ± 1.528[a]	-132.500 ± 1.000[a]
Lead	-1095.933 ± 3.219[a]	-2054.800 ± 6.245[a]	-933.900 ± 2.000[a]	86.0667 ± 1.155[b]

Results are presented as Mean ± SD. Values with different superscript alphabets across the rows are significantly different from each other at $P \leq 0.05$. Post-Hoc Test (Tukey), n = 3.

5. Discussion

One of the most traditional methods of water treatment is filtration. However, very small particles can pass through the membranes used in water filtration, meaning that not all contaminants are eliminated. This study found that filtration alone resulted in only slight improvements in most tested parameters, indicating it is not an efficient method of water purification. Activated carbons prepared from inexpensive agricultural waste have been identified as potential adsorbents for removing various pollutants from industrial wastewaters [24]. Their large surface area, low moisture and ash content suggest that the particle density is relatively small, making the biomaterial an excellent raw material for adsorbents [1].

The occurrence of heavy metals in wastewater (Table 1) could be due to the cleaning processes of floors, blenders, reactors, mixers, and packaging equipment. This finding is consistent with observations by Hashem, *et al.* [25], who detected heavy metals predominantly in wastewater from the textile, chemical, and allied industries.

The removal efficiencies of heavy metals by Maize Cob (MC) varied significantly ($p < 0.05$) as shown in Table 2. The wastewater sample from DICON Company had the highest adsorption rate for Zn2+ (92.200 ± 0.954). MC reduced Cu2+ in wastewater from BAM-PAINT Company by 40%, while NBC wastewater had the highest Cd2+ ion adsorption rate at 94%. MC absorbent reduced Ni2+ by 72% and Pb2+ by 98% in NBC wastewater.

This study supports other research indicating that agricultural wastes can be used as adsorbents for removing Cd (II), Cu (II), Pb (II), and Zn (II) ions from aqueous solutions [26]. Studies have shown the variability of inexpensive biomass developed and commercialized for pollution control. Reported the use of ash from agricultural products to remove Pb2+ ions from water. Other research has found that agricultural materials like maize cob, groundnut husk [27-29], sawdust, spent mushroom substrates [30], rice bran, soybean, cottonseed crop milling waste, jute, and leaf-derived biosorbents [31, 32] are efficient, eco-friendly, and economical biosorption methods for heavy metal pollution. According to Bashir, *et al.* [33] and Escudero, *et al.* [34], biosorption is attractive for removing metal ions due to its easy accessibility, selectivity, efficiency even at low concentrations, minimal production of secondary sludge, and cost-effectiveness.

The effectiveness of Maize Cob Charcoal (Table 3) in removing heavy metal ions can be attributed to the porosity of the carbon structure and the variety of surface functional groups Al-Malack, *et al.* [35]. The values from this study align with Al-Malack, *et al.* [35], who found adsorption efficiencies of 78% and 94% for Cd2+ and Pb2+ ions, respectively.

The results revealed that maize cob, an agricultural waste product, is effective in sorbing heavy metals from aqueous solutions. The sorption of all five metal ions onto unmodified maize cob is a physisorption process, while the use of ETMC (Table 4) involves a combination of physisorption, chemical ion exchange, and chemisorption processes.

Various industrial wastes also have adsorption capacities and can be used to adsorb heavy metals from wastewater. These industrial wastes are by-products and are rarely used for other purposes, making them easily available and economical. Industrial wastes such as fly ash, blast furnace sludge, waste slurry, lignin (a black liquor waste of the paper industry), iron (III) hydroxide, and red mud have been explored for their technical feasibility in removing toxic heavy metals from contaminated water [36, 37]. Several adsorbents have been used to adsorb zinc from wastewater. Some of the highest adsorption capacities reported for Zn2+ are 168 mg/g for powdered waste sludge, 128.8 mg/g for dried marine green macroalgae, 73.2 mg/g for lignin, 55.82 mg/g for cassava waste, and 52.91 mg/g for bentonite [36, 37].

6. Conclusion

In conclusion, results obtained from the study showed that heavy metals identified in the waste water samples collected from industries located in Kaduna South and Chikun local government areas include Zn^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+} and Cd^{2+}. MC and MCC were most effective in eliminating Pb^{2+} in all the samples except for NBC waste water. Meanwhile, Zn^{2+} was actively removed from BAM-PAINT and NBC waste water followed by Ni^{2+} in CHELLCO industrial waste water. ETMC had the highest effect on heavy metal ions removal in all the industrial waste water samples. This study has therefore, demonstrated that Maize Cob, Maize Cob Charcoal and Ethylene-diamine-disuccinate treated maize cob are effective absorbent for elimination of lead, zinc, cadmium, nickel and copper in waste water from Kaduna State, Nigeria.

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