Utilizing Modified Maize Cobs as an Agricultural Waste Adsorbent for Removing Zinc (II) and Chromium (VI) Ions from Wastewater

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Abstract

The purpose of this study is to investigate the use of maize cob carbon powder as an adsorbent for the removal of zinc (II) and chromium (VI) ions from industrial effluent. The non-degradable and toxic nature of these metal ions make their removal from wastewater crucial prior to discharge into the environment. Despite the many techniques that have been developed for the removal of heavy metals, many have proven to be inefficient, generate sludge, and are expensive. Adsorption processes have been shown to be one of the most efficient methods for the removal of toxic metal ions from contaminated water. Activated carbon is commonly used for this purpose but is expensive. Considering this, the search for more economical and safe options has led to the investigation of low-cost adsorbents as alternatives to activated carbon. In this study, maize cob carbon powder was chosen as the adsorbent due to its low cost, non-toxicity, and availability. A batch experimental approach was utilized to investigate the effects of temperature, pH, adsorbent loading, contact time, and initial metal ion concentration on the adsorption process. The results of the study indicate that maize cob carbon powder can be effectively used as an economical adsorbent for the treatment of contaminated water.

1. Introduction

An increase in population due to factors such as birth rate, migration, and development has led to a high demand for agricultural and industrial goods. This has resulted in rapid industrialization and increased industrial activity. In underdeveloped countries, this has led to indirect or direct exposure to pollution from heavy metals, such as lead, chromium, iron, cadmium, nickel, copper, selenium, cobalt, vanadium, mercury, arsenic, and zinc (Renu et al., 2017). These heavy metals are primarily released into the environment by industries such as tanneries, mining, fertilizer production, textiles, metal plating, paper mills, battery production, refineries, paint, pesticides, and other chemical production. The direct release of sewage from these industries, hospitals, and other sources into water bodies is identified as a major cause of environmental pollution. Some of these toxic metal ions present in industrial effluents have been found to be teratogenic, mutagenic, or carcinogenic (Su 2014, Basha et al., 2008).

In recent years, there has been a growing concern over the increasing levels of heavy metal pollutants in wastewater. This has led to a need for effective and affordable wastewater treatment methods. Modified maize cobs have been identified as a potential agricultural waste material for removing heavy metal ions from wastewater. The study will analyse the various modification methods used for maize cobs, and the impact of these modifications on the removal efficiency of zinc and chromium ions. The results of previous studies will be compared and evaluated to provide an overview of the current state of knowledge in this field.

Conventional treatment technologies for heavy metals removal commonly used includes reverse osmosis, ion exchange, oxidation, reduction, electrodialysis, chemical precipitation, ultrafiltration etc. (Hegazi, 2013). However, they have their intrinsic restrictions such as incomplete metal ions removal, sludge generation, inefficient, sensitive operating conditions, high operating cost, and high cost of sludge
disposal. Adsorption technique has proving to be the most thriving method of toxic ions removal technology, due to the effectiveness, binding ability of various agricultural waste, and its possible marketing gains ahead of other techniques of contaminated water treatment (Saravananan et al., 2016). The high assimilation efficiency of agricultural by-product is ascribed to phenolic, carbonyl, sulfhydryl, and amino functional sets (Renu et al., 2017). The assimilation system steps of Agricultural adsorbent inclusive of complexation, chemisorption, adsorption on surface, diffusion through pores and ion exchange. Exploring the agricultural by-product has included wastes like eggshell, rice chaff, wheat bran and chaff, lemon peels, orange peels, lime peels, apple peels, and peels of banana, tree barks, shells of groundnut, coconut, hazelnut and walnut, tea waste and leaves of Cassia fistula, sugarcane bagasse, soybean and cotton seed hulls, cotton stalk etc. (Alalwan et al., 2020). Some of these agricultural by-products have exhibits promising withdrawal efficiency for toxic metal ions from polluted water either in their ordinary formation or after some Chemical or physical modifications (De Gisi et al., 2016).

The novelty of the study lies in the use of modified maize cobs as a potential agricultural waste material for removing heavy metal ions from wastewater. The study aims to analyze various modification methods used for maize cobs and the impact of these modifications on the removal efficiency of zinc and chromium ions. The analysis also highlights the limitations of conventional treatment technologies for heavy metal removal and the effectiveness of the adsorption technique. The research focus on the efficiency of maize cobs carbon powder for the removal of Zinc (II) and chromium (VI) ions from synthetic wastewater and the examination of various factors affecting the adsorption process such as contact/incubation time, initial pH, adsorbent loading, initial metal ion concentrations and change in temperature. The work is aimed at finding a readily available, efficient, cheap, and acceptable solution for wastewater treatment.

2. Methodology And Material Used

2.1 Collection and Adsorbents Preparation

**Maize cobs:** In this paragraph described a protocol to produce modified maize cobs powder. The raw material, maize cobs, were sourced from a specific location within the Nile University of Nigeria (N 9°0'37.566", E 7°23'38.33412°). The cobs were cleaned by washing with tap water and rinsing with double-distilled water to remove contaminants. The cobs were then dried in an oven at a temperature of 103°C for 2 hours. Subsequently, the cobs were carbonized by burning without allowing them to turn to ashes, cooled, and crushed using a grinder as shown in Figure 1. The resulting powder was sieved to remove particles larger than 1mm, washed multiple times using purified water, and oven-dried to constant mass at 103°C for 2 hours. The dried powder was then heated in a muffle furnace at 500°C for 1 hour and 30 minutes, cooled, and its bulk density and specific gravity were measured. Finally, the modified maize cobs powder was stored in a container in a desiccator to maintain its stability.

2.2 Synthetic Wastewater Preparation
Preparation of Stock solutions: In accordance with Figure 2, a stock solution of 1000 mg/L of Chromium (VI) ions and Zinc ions was prepared by dissolving 2.835 grams of 99.9% analytical-grade Potassium dichromate ($K_2Cr_2O_7$) and 4.424 grams of 99% analytical-grade Zinc Sulphate ($ZnSO_4\cdot7H_2O$) in 1000 milliliters of purified (distilled) water within a 1000 milliliter volumetric flask under laboratory conditions. To adjust the solutions' pH to 2.02, 3.11, 4.22, 5.41, 6.28, 7.02, 8.31 and 9.05, Hydrochloric acid and Sodium hydroxide were utilized. An initial concentration of 20 mg/L was used for the various pH values, and distilled water was employed throughout the experimental studies. Synthetic Wastewaters (standard solutions) containing chromium and Zinc ions at concentrations of 10, 20, 30, 40, 50 and 60 mg/L were prepared using the following equation.

$$S_1V_1 = S_2V_2$$  \hspace{1cm} (1)

$S_1$ = conc. of stock solution (e.g., 1000mg/L)

$V_1$ = vol. to be taken from stock solution (unknown)

$S_2$ = conc. of standard solution (e.g., 10mg/L)

$V_2$ = vol. of standard solution (e.g., 100mL)

2.3 Adsorption Investigation

A batch experimental protocol was employed to investigate the adsorption capacity of modified maize cobs powder for Chromium and Zinc ions. The impact of pH, initial ion concentration, temperature, contact time, and adsorbent loading on the wastewater was studied. The initial and final concentrations of the prepared synthetic wastewater were determined using an AA spectrometer (ICE 3000 series, UK) at the Sheda Science and Technology Complex (SHESTCO). The initial pH values of all the varying concentrations and that of the modified cobs powder were measured using a HI9829 Multiparameter instrument (Romania) at the Civil Engineering Environmental laboratory, Nile University of Nigeria. To analyze the effects of the various factors, some parameters were kept constant while others were varied. For example, 20mg/L initial concentration, 180 rpm, 100mL sample volume, and 4g/L adsorbent dosage were used to study the effect of pH, contact time, and temperature.

Synthetic wastewater with a concentration of 20mg/L of Chromium (IV) and Zinc (II) ions were utilized to study the effects of pH, temperature, contact time, and adsorbent dosage on the adsorption process. Solutions with concentrations of 10, 20, 30, 40, 50, and 60mg/L of Chromium and Zinc ions were used to evaluate the effect of initial ion concentration on adsorption. Adsorbent doses of 2, 4, 6, 8, and 10g/L were employed to investigate the effect of adsorbent dosage on the removal of Chromium and Zinc ions.

A series of experiments were conducted using 250ml flasks containing 4g of adsorbent and 100ml of synthetic wastewater with varying pH values (2.02 to 9.05) and an initial concentration of 20mg/L of Chromium and Zinc ions. The mixture of maize cob powder and wastewater was agitated for 180
minutes at 28.6°C and 180 rpm using a Laboratory companion shaker (SK-300 model) for both Chromium and Zinc ions. Following the specified contact time, the mixture was filtered using filter papers. The final concentration of the solution was then determined using AAS at the maximum adsorption wavelength. These steps were repeated for the effects of temperature, adsorbent dosage, initial ion concentration, and contact duration, with some factors held constant and others varied.

The percentage withdrawal of Zinc (II) and Chromium (VI) ions from the polluted water were computed by the following equation.

\[
\text{Percentage Removal (\%)} = \left( \frac{C_i - C_e}{C_i} \right) \times 100
\]

(2)

Where, \(C_i\) is the initial and \(C_e\) is the remaining ions (mg/L) in the fluid.

Equilibrium withdrawal capacity for each sample was computed using equation 3 below.

\[
\text{Adsorption capacity (mg/g) } q_e = \frac{(C_i - C_e)V}{w}
\]

(3)

Wherein, \(C_i\) means the initial and \(C_e\) means the final ions after stability in mg/L.

\(w\) stands for weight of absorbent used in g and \(V\) stands for volume of wastewater used in L.

The effects of pH (2 to 9), temperature (28.6 to 55°C), contact time (30 to 300 min) and initial ion concentrations (10 to 60 mg/L) on uptake of the metals were also examined.

3. Result And Discussions

3.1 Consequence of Parameters on Chromium and Zinc Metals

3.1.1 Consequence of pH

Figure 3 illustrates that the efficiency of adsorption for Zinc (II) and Chromium (VI) ions in polluted water is greatly influenced by the pH of the wastewater. The results demonstrate that the removal of Cr and Zn ions increased to a peak level and then decreased as the pH range changed from 2 to 9, at a temperature of 28.6°C and a shaking rate of 180 rpm. The highest percentage of Cr (VI) removal was 82.75% at pH 4.22, while the highest percentage of Zn (II) removal was 94.75% at pH 7.02. The pH of the system controls the adsorption capacity by impacting the surface properties of the adsorbent and the forms of Chromium ions present in the wastewater (Garg et al., 2007). Studies by Yu et al., (2003) using sawdust as an adsorbent found that maximum adsorption occurred at pH 5, while Saravanan et al., (2016) observed that the highest withdrawal of Chromium (IV) ions by custard apple seeds was at pH 3. Daneshvar et al., (2002) reported that there is an inverse relationship between the adsorption of Chromium by soya cake and pH. When the pH is lower than neutral, Zinc ions mainly undergo the
adsorption process. Zinc ions begin to precipitate as Zn (OH)$_2$ when the pH increases above neutral, as established by (Karthikeyan et al., 2004).

### 3.1.2 Consequence of Temperature

The temperature had a significant impact on the adsorption of Chromium and Zinc ions onto modified corn cobs powder. The effect of temperature on the removal of Cr and Zn ions using maize cobs carbon powder was investigated within a temperature range of 28.6 to 55°C, while maintaining other parameters constant. As the temperature increased from 28.6 to 55°C, the percent removal of Cr ions increased from 55.5% to 93.05% and then decreased from 93.05% to 79.4% (Fig.4). The maximum removal percentage of Chromium (VI) was thus found to be 93.05% at pH 4.22 and a temperature of 40°C. For Zinc, the percent removal decreased from 94% to 63.8% as the temperature increased from 28.6 to 55°C, indicating that Zinc adsorption was higher at lower temperatures. Figure 4 illustrates that lower temperatures do not favor Chromium ion removal but are favorable for Zinc ion removal. The adsorption ability is inversely proportional to the temperature, which may be due to the reduction in adsorptive intensity between the metal ions and the functional sites on the adsorbent surface (Abdel et al., 2011, Guo et al., 2002).

### 3.1.3 Consequence of Contact Period

From Figure 5, it can be seen that there is an increase in the adsorption of Zinc and Chromium ions as the contact time is prolonged before reaching equilibrium. The results show that the removal of Cr (VI) ions increased from 49.5 to 92.1% as the contact time varied from 30 to 240 minutes. Also, from 240 to 300 minutes, the adsorption percentage of Cr (VI) remained unchanged at 92.1%. Similarly, it was observed that the adsorption of Zn (II) ions increased from 50.55 to 95.35% as the contact time varied from 30 to 180 minutes, and remained unchanged at 95.35% from 180 to 300 minutes. This suggests that equilibrium was reached at 240 and 180 minutes for Cr and Zn ions, respectively. Gupta et al., (2010) found equilibrium point after 70 minutes using fertilizer industry waste as an adsorbent, however, in this study, the equilibrium point was found to be higher. Studies on calcined eggshell, eggshell, modified wheat bran, and wheat bran found that the withdrawal rate of Cr (VI) ions increases with the extension of the adsorption time but remained constant after a stable period of 300 minutes (Renu et al., 2017). Kaushal and Singh, (2017) reported that stability was achieved at 1 hour for mango tree leaves and 1 hour 20 minutes for Ashok and bel tree leaves, after which the amount of zinc metal ions in the suspension remained stable.

### 3.1.4 Consequence of Adsorbent Loading

The uptake of Chromium and Zinc ions was dependent on the adsorbent loading. The effectiveness of Chromium (VI) and Zinc (II) removal was measured by varying the adsorbent loading from 2 to 12 g/L while maintaining other parameters constant. As shown in Figure 6, it was observed that the adsorption effectiveness of Chromium and Zinc increased as the adsorbent dose increased. This increase in Chromium and Zinc removal can be attributed to an increased surface area and the availability of more sorption sites on the sorbent material (Kashefi et al., 2012, Kaushal et al., 2016). Hu et al., (2010) also
found that Jatroha oil cake and sugarcane bagasse were effective in Chromium (IV) uptake, with maximum removal of 97% and 92% obtained at an adsorbent dose of 20g/L. Guo et al., (2002) also reported that mango and ashok leaves were able to absorb Zinc ions up to 74 and 77% at a dosage of 12g/L but higher increases in the dose did not result in additional percentage removal. Gupta et al., (2010) concluded that high adsorbent doses may lead to low sorption ability due to the decrease in the availability of higher energy sites occupied by a larger fraction of lower energy sites. The highest percentage of Zn (II) and Chromium (VI) removal was about 86.2 and 96.5% at dosages of 8 and 6g/L respectively, indicating that stable conditions were achieved at these dosages. As more adsorbent is added, the amount of ions not bound to the adsorbent remains constant, as does the amount of ions bound to the adsorbent.

### 3.1.5: Consequence of Initial Zn (II) & Cr (VI) Ions Concentration

The effect of initial chromium and zinc ions concentration on their removal rate was studied within the range of 10, 20, 30, 40, 50, and 60 mg/L, under varying pH values of 4.22 and 7.02, temperatures of 40 and 28.6 °C, contact times of 240 and 180 min, and with adsorbent doses of 8 and 6 g/L for Cr and Zn, respectively. Results from Figure 7 indicate that an increase in initial concentration leads to a decrease in the percentage of removal. The percentage removal was found to be greater than 96% and 98% at initial Cr(VI) and Zn(II) concentrations of 10 mg/L, respectively, but as the concentration increased, the percentage removal decreased. This can be attributed to the exhaustion of adsorption sites at higher initial metal ion concentrations. This is consistent with the findings of Yu et al. (2003) that the equilibrium concentration is affected by both the initial metal concentration and the adsorption rate of the metal ion. The availability of sites for adsorption is limited at high initial metal ion concentrations (Kaushal et al., 2016). Additionally, a high initial metal ion concentration creates a strong driving force that overcomes the resistance of ions in the mixture to bulk exchange (Babel and Kurniawan, 2003, Ong et al., 2004).

### 3.2 Adsorption models

Freundlich and Langmuir isotherm models were made use of to explain the stability established uniting final concentration ($C_e$) and adsorption capacity ($q_e$). The result of adsorption studies fitted well with Langmuir isotherm for both chromium (Fig 8) and zinc (Fig 9) based on the highest values of correlation coefficient ($R^2$) of 0.999 and 0.996.

### 4. Conclusions

The findings of this study demonstrate that maize cob carbon powder can be effectively utilized as a sorbent material for the removal of toxic metal ions, such as zinc (II) and chromium (VI), from wastewater. The widespread cultivation of corn in West African countries provides an ample supply of this material. The use of corn cob as a sorbent material is environmentally friendly, as it can be sourced from agricultural waste and is accessible even in low-income countries. The batch adsorption
experiments were conducted by varying parameters such as temperature, pH, sorbent loading, contact time, and initial metal ion concentration. Summary of findings given Table 1.

### Table 1. Summary of the Findings on Maize Cob Carbon Powder as a Sorbent Material

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Optimal Values</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.22 and 7.02</td>
<td>Highest removal efficiency observed</td>
</tr>
<tr>
<td>Temperature</td>
<td>40°C and 28.9°C</td>
<td>Highest removal efficiency observed</td>
</tr>
<tr>
<td>Sorbent Loading</td>
<td>8 and 6 g/L</td>
<td>Highest removal efficiency observed</td>
</tr>
<tr>
<td>Contact Time</td>
<td>240 and 180 min</td>
<td>Highest removal efficiency observed</td>
</tr>
<tr>
<td>Initial Metal Ion Concentration</td>
<td>10 mg/L (for chromium and zinc ions)</td>
<td>Highest removal efficiency observed</td>
</tr>
<tr>
<td>Adsorption Isoterm</td>
<td>Langmuir</td>
<td>Highest removal efficiency observed</td>
</tr>
</tbody>
</table>

In conclusion, this study highlights the potential of maize cob carbon powder as an effective sorbent material for the removal of toxic metal ions, such as zinc (II) and chromium (VI), from wastewater. The availability of corn cob as an agricultural waste in West African countries and its environmental friendliness make it an accessible and sustainable option for wastewater treatment. The results of the batch adsorption experiments indicate that the highest removal efficiency was observed under specific conditions, such as pH, temperature, sorbent loading, contact time, and initial metal ion concentration. The Langmuir adsorption isotherm for the two metals, Zn and Cr, was in good agreement with the experimental data. Thus, maize cob carbon powder presents an economical and environmentally friendly solution for the treatment of contaminated water.

### Declarations

#### Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Authors' contributions

Begmyrat Kulmedov was responsible for Conceptualization, Methodology, Resources, Writing - Review & Editing, Supervision, and Project administration.
Ado Mohammed was responsible for Software, Validation, Formal analysis, Investigation, Writing - Original Draft.

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Availability of data and materials

Data and materials are available upon request.

References


Figures
Figure 1

Preparation of adsorbent

Figure 2
Synthetic wastewater Preparation

Figure 3
Consequence of pH on adsorption of Zinc and Chromium

Figure 4
Consequence of Change in temperature on sorption of Zinc and Chromium ions
Figure 5

Consequence of contact period on adsorption of Zn (II) and Cr (VI) ions

Figure 6

Consequence of adsorbent loading on sorption of Zn and Chromium ions
Figure 7

Consequence of initial Concentration for Cr & Zn ions on their withdrawal

$$y = 5.2334x + 0.7683$$
$$R^2 = 0.9993$$

Figure 8

Langmuir (a) and Freundlich (b) isotherms of chromium (IV) on Maize cob carbon powder

$$y = 0.572x - 0.702$$
$$R^2 = 0.983$$
Figure 9

Langmuir (c) and Freundlich (d) isotherm model of Zinc (II) on Maize cob carbon powder.