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Research Article

Treatment of oilseed industrial wastewater using corncob modified with NaOH as an adsorbent under a fixed bed column

Yushau Muhammad Salis, Aliyu Adamu Dandajeh*

ABSTRACT: The treatment of industrial wastewater is a source of environmental concern due to the presence of various pollutants that could have detrimental effects on ecosystems and human health. This research aims to investigate the potential of using corncob treated with 1M NaOH as an adsorbent for the removal of pollutants from wastewater collected from Sunseed Nigeria Limited. Corncob, a byproduct of the agricultural waste, has shown capability as an adsorbent due to its high surface area and availability at low cost. The research involved the preparation of corncob adsorbent and its characterization using technique; Fourier-transform infrared spectroscopy (FTIR). Adsorption experiment was conducted using continuous study by a fixed bed column with a 5.0 cm internal diameter and a height of 45cm, to evaluate the efficiency of corncob in removing pollutants from oil seed industrial effluent. The initial concentrations of the pH, TSS, DO, BOD, COD, Lead and Cadmium were examined to be; 4.8, 360 mg/L, 110 mg/L, 40 mg/L, 7000 mg/L, 1.268 mg/L and 0.138 mg/L, respectively. The best removal efficiency for cadmium and lead were: 65.94% and 94.01%, respectively at pH of 6.5 and contact time of 6hrs. Furthermore, the removal efficiency for TSS, BOD, and COD were: 20%, 55% and 57.14%, correspondingly. It was therefore concluded that corncob has proven to be a potential material for the treatment of physico-chemical pollutants from industrial effluent. It is recommended that the corncob should be utilized in large amounts for the treatment of industrial effluents.

Keywords: *Adsorbent, Corncob, Pollutants, Wastewater, Removal efficiency*

1. INTRODUCTION

The growing global demand for vegetable oils as a results of population increase has resulted in an attendant increase in the generation of oilseed effluent pollutants [1, 2]. This discharge, characterized by high concentrations of organic matter, including oil and grease, chemical oxygen demand (COD), biochemical oxygen demand (BOD) and heavy metals poses a significant hazard to environment, aquatic ecosystems and human health if released untreated [3, 4]. It is important to note that among all the pollutants, heavy metals are most hazardous as they are non-biodegradable and persist in the environment and could lead to cancer [5, 6, 7, 8]. However, despite widespread efforts to reduce their release into the environment, heavy metal pollution remains a significant problem [9]. Furthermore, the elevated levels of organic pollutants deplete dissolved oxygen, leading to eutrophication and unsettling aquatic life. Likewise, untreated wastewater could contaminate groundwater resources, impacting potable water supplies [10].

Various Similarly, conventional wastewater treatment technologies, such as coagulation-flocculation, activated sludge processes, and membrane filtration, have demonstrated varying degrees of effectiveness in treating oilseed wastewater. However, these methods often suffer from limitations including high operational costs, significant energy consumption, and the generation of secondary pollutants in the form of chemical sludge [11, 12]. Consequently, there is a growing need for cost-effective, environmentally friendly, and sustainable alternatives for oilseed wastewater

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Similarly, conventional wastewater treatment technologies, such as coagulation-flocculation, activated sludge processes, and membrane filtration, have demonstrated varying degrees of effectiveness in treating oilseed wastewater. However, these methods often suffer from limitations including high operational costs, significant energy consumption, and the generation of secondary pollutants in the form of chemical sludge [11, 12]. Consequently, there is a growing need for cost-effective, environmentally friendly, and sustainable alternatives for oilseed wastewater treatment. Therefore, it is essential to find a new strategy and sustainable methods to treat the industrial wastewater [13].

Hence, such can be achieved using cheap and abundant natural materials which are characterized by high efficiency as adsorbents in the form of activated carbon [14, 15, 16]. Likewise, [17] reported that some agricultural wastes such as wood sawdust, rice husk, corncob and charcoal were used to treat the wastewater to avoid environmental accumulation.

Moreover, adsorption has emerged as a promising technology for the removal of pollutants from wastewater due to its simplicity, efficiency, and potential for the use of readily available and low-cost materials [18, 19]. In recent years, considerable attention has been directed towards the utilization of agricultural waste materials as adsorbents, capitalizing on their abundance, biodegradability, and inherent adsorptive properties [20]. Also, among the various agricultural residues studied, corncob, a lignocellulosic biomass derived from maize, holds considerable potential as an adsorbent for wastewater treatment.

Corncob is an abundant and cheap agricultural byproduct generated in large quantities worldwide and Zaria-Nigeria, where this study was carried out [21]. Its inherent porous structure, high cellulose and hemicellulose content, and the presence of various functional groups such as hydroxyl and carboxyl make it a suitable precursor for the preparation of effective adsorbents [22]. In addition, while raw corncob exhibits some adsorptive capacity, modification through physical or chemical activation can significantly enhance its surface area, porosity, and affinity for specific pollutants.

This study therefore, investigated the potential of corncob, chemically modified using 1M NaOH as an adsorbent for the treatment of oilseed industrial effluent collected from Sunseed Nigeria Limited using a column experiment. The research aims to remove TSS, COD, BOD, lead and cadmium from the wastewater, which are source of concerns to the oil seed industry and the inhabitants surrounding the industry. The findings of this research are expected to provide valuable insights into the viability of utilizing corncob as a sustainable and cost-effective alternative, contributing to the development of environmentally responsible solutions for industrial wastewater management. This could take care of the growing concerns on the generation of waste products generated by the concerned industry and their eventual discharge or release issues therein, hence the need for this study.

2. MATERIALS AND METHODS

2.1. Materials. 2.1.1. Apparatus/Equipment. The apparatus/equipment used in this study are: measuring cylinder (500mL), volumetric flask (1000mL), conical flask (300mL), beaker (400mL), funnel, washing bottles, magnetic stirrer, sample bottle, petri dish, oven, desiccator, sieves (0.425mm), plastic bottle, grinder, refluxing bottles, Fourier-Transform Infrared Spectroscopy (FTIR), Atomic Adsorption Spectrometer (AAS), crucible, gallon, gloves, mortar & pestle, detergent, BOD bottle, COD machine, pH meter, incubator, pipette and weighing balance.

2.1.2. Chemical reagents. The chemical reagents used in this study are: oil seed industrial effluent, NaOH (1M), distilled water, corncobs, H_2SO_4, starch solution, $Na_2S_2O_3.5H_2O$, Alkali-iodide-azide reagent, $MnSO_4$, $HgSO_4$, ferroin indicator, $Fe(NH_4)_2(SO_4)_2$ and K_2Cr_2O7.

2.1.3. Parameters. The physical and chemical parameters measured in this study are: pH, Dissolved Oxygen (DO), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), lead and cadmium.

2.2. Methods. ***2.2.1. Corncobs collection.*** The corncob was collected from local market in Shika, Giwa Local Government Area of Kaduna State, Nigeria and conveyed to the Environmental Engineering Laboratory, Department of Water Resources and Environmental Engineering, Ahmadu Bello University, Zaria-Nigeria for investigation.

2.2.2. Preparation of the corncob adsorbent. The corncob was crushed by mortar and pestle, then washed with distilled water by mixing it in a shaker for 24 hours in order to remove impurities from the sample [23]. The cleaned corncob was placed into a large glass baking dish and dried at room temperature, after which, it was sieved using a 0.425mm sieve size. Consequent upon that, 350g of the corncobs was chemically modified with 700mL of 1M NaOH for 1hour. The modified corncob was washed with de-ionized water until the pH was 7, after which, it was dried in the oven at 100°C for 1 hour. The corncob adsorbent was stored in pre-clean air tight plastic bottles and kept for the experiment. The yield of the Corncob adsorbent was determined using equa-

$$\text{The yield of the corncob} = \frac{W_1}{W_2} \times 100 \quad (1)$$

Where, W_1 and W_2 are the modified and unmodified weights of the corncob. The concorb unmodified (rawmaterial) and modified are shown in Figure 1.

2.2.3. Laboratory column design. The adsorption experiment was carried out in a transparent plastic column with a 5.0 cm internal diameter and a height of 45cm as shown in Figure 2. The adsorbent was confined in the column by fine faucet material at the bottom and a glass beds layer packing at the top of the adsorbents to ensure a uniform distribution of the influent (oilseed effluent) through the adsorbent. The influent is introduced to the column through a rubber stopper, fixed at the top of the column and controlled by a valve at the lower end of the column. A 5 litre plastic container used as the feeder at the top of the column and a 1 litre glass container was used as a sample treated reservoir at the bottom of the column. Figures 2 depicts the experimental set up diagrams for the column adsorption study. The removal efficiency of the adsorbent was determined using equation (2) as reported by [24]:

$$\%\ \text{removal efficiency of the metal ions} = \frac{Co - Ce}{Co} \times 100 \quad (2)$$

Where, Co and Ce are the initial and residual concentrations (mg/L) of the parameters, respectively. The removal efficiency (%) reveals the percentage of the pollutant in question removed in relation to its original concentration from the wastewater. The adsorption capacity was computed by using the mass balance equation (3) as reported by [4]:

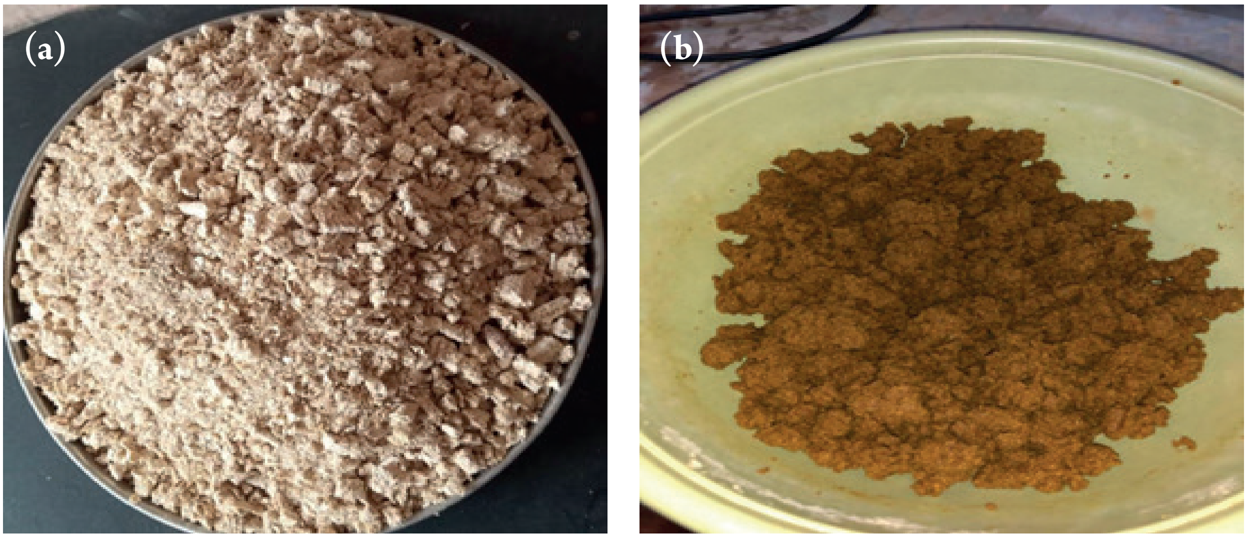

Figure 1. Corncob powder: (a) without modification, (b) modified with NaOH.

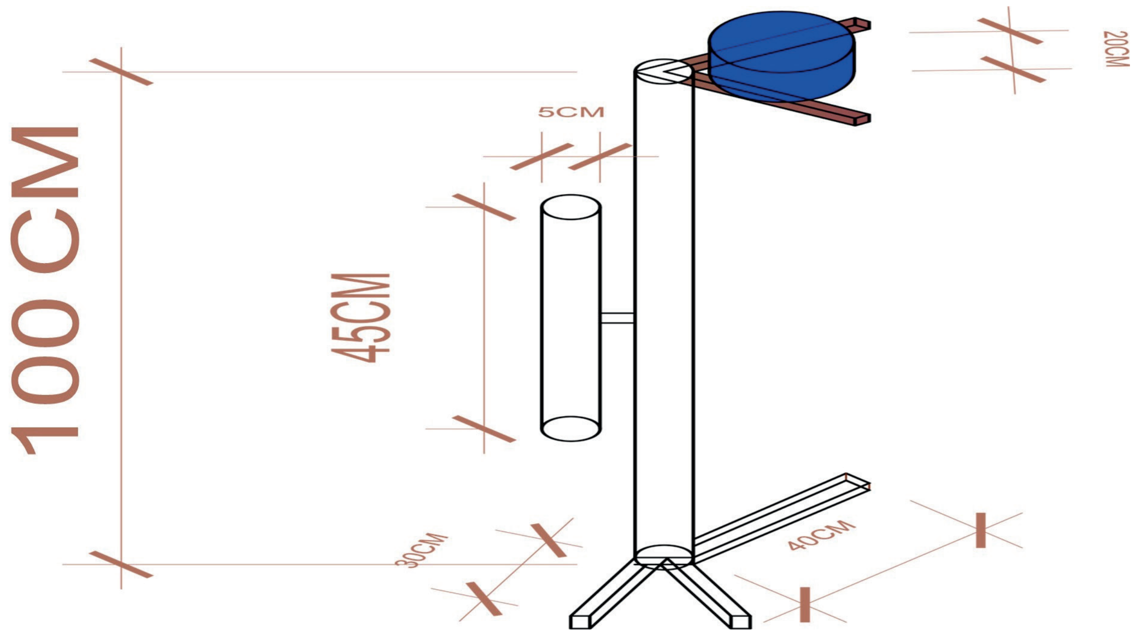

Figure 2. Schematic of the column experimental setup.

$$\text{Adsorption capacity } q = \frac{(Co - Ce)V}{W} \quad (3)$$

Where, q is the adsorption capacity in (mg/g), V is the volume of ions solution (L) and W is the mass of corncob (g), Co and Ce as previously defined. It indicates the amount of the adsorbate (pollutant) adsorbed or removed by the adsorbent per gram of the adsorbent from the wastewater. Figure 3 depicts the schematic presentation of the corncob adsorbent production.

3. RESULT AND DISCUSSION

The characterization of the oilseed effluent is depicted in Table 1. The table indicates the initial concentrations of pH, Total Suspended Solids (TSS), Dissolved Oxygen (DO), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), lead and cadmium.

The primary concentrations of pH, Total Suspended Solids (TSS), Dissolved Oxygen (DO), Biochemical Oxygen Demand

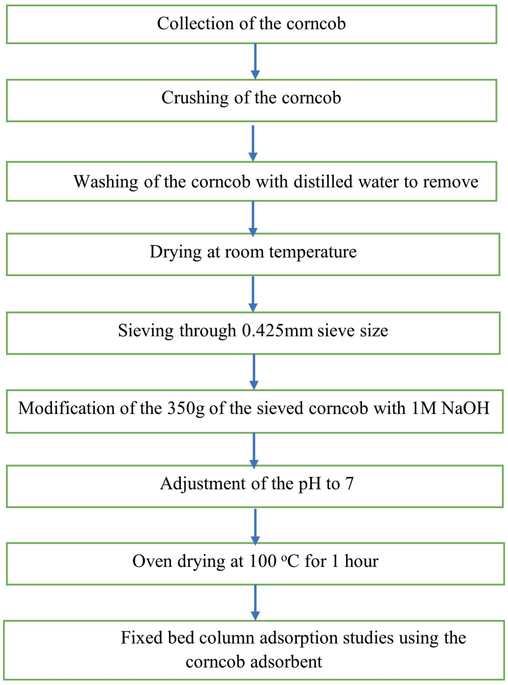

Figure 3. Schematic presentation of the corncob adsorbent production and adsorption studies.

Table 1. Concentrations of the oil seed wastewater before treatment with corncob.

Parameters	Concentrations	Standard for discharge into streams
pH	4.8	6-9
TSS (mg/L)	360	30
DO (mg/L)	110	8-9
BOD (mg/L)	40	50
COD (mg/L)	7000	80
Lead (mg/L)	1.268	<1
Cadmium (mg/L)	0.138	<1

(BOD), Chemical Oxygen Demand (COD), Lead, and Cadmium were established to be; 4.8 mg/L, 360 mg/L, 110 mg/L, 40 mg/L, 7000 mg/L, 1.268 mg/L, and 0.138 mg/L, respectively as shown in Table 1. It is observed that some of the parameters were above the standard for the discharge of effluents into the receiving streams. This would certainly have negative impact on both the environment and aquatic organisms, signifying the need for treatment before eventual discharge of the effluent. The DO, BOD and Cd concentrations are within the permissible limits; while the pH, TSS, COD and Lead were above the permissible limit. The elevated BOD and COD values of 40 mg/L and 7000 mg/L indicate high organic and refractory pollutions, depleting oxygen levels and degrading the receiving water quality. Figure 4 indicates the FTIR of the untreated/unmodified corncob.

The characterization of the unmodified corncob adsorbent using Fourier Transform Infrared Spectroscope (FTIR) is depicted in Figure 4. The FTIR of the untreated corncob revealed the presence of several functional groups which include: carboxylic acids (indicating the presence of organic acids in the corncob), alkynes (indicating the existence of carbon-carbon triple bonds in the corncob) and the presence of aromatic functional group, suggesting the existence of the aromatic compounds in the corncob.

Furthermore, [25, 26, 23] reported the peak stretches between 2800 and 3500 cm^{-1} to be attributed to hydroxyl (OH). Equally, the peaks at 2031.4 and 1513.3 cm^{-1} could reveal the presence of alkynes and aromatic functional groups. Similarly, the peaks at 1636.3, 1428.8, 1364.2 cm^{-1} could signify the existence of amines, aromatic and alkyls functional groups. Also, the peaks at 1241.2 to 760.4 cm^{-1} could be attributed to alkyl halides.

Correspondingly, the existence of amines indicates the presence of nitrogen-containing compounds in the corncob. Likewise, presence of alkyls specifies the existence of alkyl chains in the corncob. In addition, alkyls are commonly found in various organic compounds and can contribute to the material's physical and chemical properties. The alkyl halides suggest the presence of halogen- substituted alkyl groups in the corncob. These observations agreed with the findings of [25].

These compounds have diverse applications, including applications as solvents, intermediates in chemical synthesis, and pharmaceutical agents. Similarly, the presence of alkenes indicates the existence of carbon-carbon double bonds in the corncob. Also, alkenes are important and could be used as starting materials for the synthesis of various compounds. Furthermore, [27, 28] reported the peak stretches between 2800 and 3500 cm^{-1} to be attributed to hydroxyl (OH).

On the other hand, Figure 5 shows the FTIR of the corncob modified with 1M NaOH. The presence of amines and alkyls indicated that the treated or modified corncob could have the ability to remove and adsorb nitrogen-containing compounds and hydrophobic organic pollutants, because amines are known to have good adsorption properties for various organic compounds; while alkyls could enhance the hydrophobicity of the material and improving its affinity for organic pollutants.

The peaks at 3280.1, 2922.2, 2050 and 1744.4 cm^{-1} could be attributed to carboxylic acid, alkanes, alkynes and ketones functional groups, respectively. Similarly, the peaks at 1509.6, 1580.4, 1408.9 and 1371.7 cm^{-1} could indicate the presence of aromatic, amines, aromatic and alkanes, correspondingly. Equally, the peaks at 1021.3 and 1155.5 cm^{-1} could reveal the existence of alkyl halides, while the peaks at 898.3 cm^{-1} could be due to the presence of alkenes functional group.

Likewise, the presence of alkyl halides indicated that the treated corncob could be used in wastewater treatment, as a precursor for the synthesis of functionalized adsorbents. It could serve as starting material for the introduction of specific functional groups onto the modified corncob, enhancing its adsorption capabilities for specific pollutants.

Equally, the existence of ketones suggests presence of carbonyl groups in the treated corncob, which may have the potential applications in wastewater treatment processes.

Comparing Figures 4 and 5, it could be deduced that the modification of the corncob with NaOH resulted to the reduction of some peaks, while some peaks were amplified. Equally some functional groups were either removed or introduced. It could be observed that, in Figure 5, the alkenes functional group had been removed from Figure 4, while alkanes and ketones functional groups had been introduced in Figure 5.

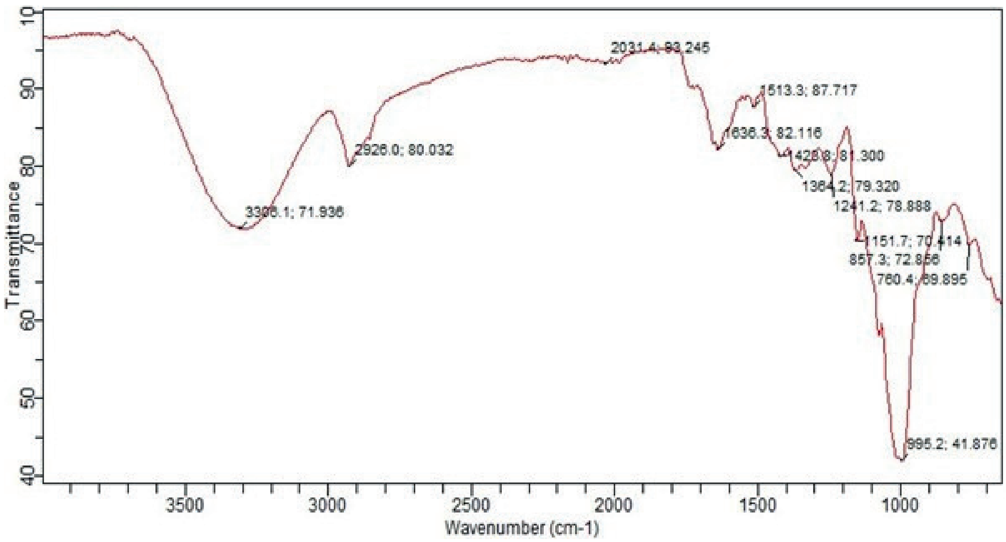

Figure 4. Indicates the FTIR of the untreated/unmodified corncob.

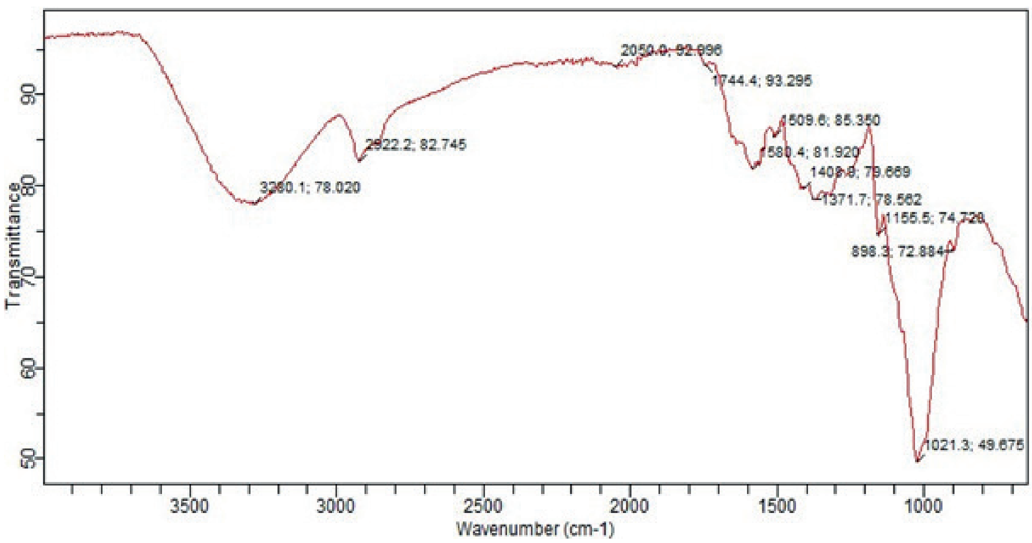

Figure 5. FTIR of the treated/modified corncob with NaOH.

The yield of the corncob activated carbon was obtained as:

$$\text{Yield} = \frac{350}{628} \times 100 = 55.71\%$$

It is important to note that the contact time of the adsorbent in the corncob adsorbent and the oilseed effluent in the column was 6 hours. Table 2 shows that the BOD, COD, lead and cadmium concentrations were decreased to 18, 3000, 0.075 and 0.047 mg/L, respectively, signifying a percentage reduction by: 55. 00%, 57.14%, 94.09% and 65.94%, correspondingly; with relative adsorption capacities of 0.2978, 54.140, 0.0165 and 0.0012 mg/g. The Table 2 also shows increase in pH value from 4.8 to 7.52, suggesting the neutralization of the oilseed effluent to a fairly alkaline value due the modification of the corncob adsorbent with 1M NaOH. The presence of the hydroxyl (OH) functional group that occurred due the impregnation of the corncob with 1M NaOH, impart alkalinity to the adsorbent, making it to have an acceptable pH value of 7.52 for discharge into the receiving streams.

Furthermore, the TSS concentration increased from 360 mg/L to 450 mg/L. The increase in TSS could be attributed to the introduction of solutes associated with the corncob adsorbent. But that did not negate the function of the corncob adsorbent in the treatment of the oilseed industrial effluent as evidenced in the reductions of the BOD, COD, lead and cadmium concentrations. This observation also confirmed the findings of [28].

Table 2. Efficiency of the Corncob in the treatment of the Oilseed effluent (t = 6 hours).

Parameters	Initial concentrations	Final concentrations	Removal efficiency (%)	Adsorption capacity (mg/g)
pH	4.8	7.52	-	-
TSS (mg/L)	360	450	20.00	1.2182*
BOD (mg/L)	40	18	55.00	0.2978
COD (mg/L)	7000	3000	57.14	54.140
Lead (mg/L)	1.268	0.075	94.09	0.0165
Cadmium (mg/L)	0.138	0.047	65.94	0.0012

*final concentration was greater than initial concentration

Table 3. Some previous works on adsorbents.

Adsorbent	Pollutant adsorbed	q_{max} (mg/g)	References
Peanut shell	Cr (III)	27.86	[31]
Orange peel	Pb (II)	204.5	[32]
Potato peel	Ni (II)	13.09	[33]
Rice husk	Methylene blue	40.6	[34]
Olive stones	Cd (II)	0.575	[35]
Broad bean peels	Methylene blue	192.7	[36]
Sugarcane bagasse	Pb (II)	5.9895	[37]
Rice husk	Pb (II)	0.1478	[38]
Corn cob	Pb, Cd	0.0165, 0.0012	This study

In a study carried out by [9] on corncob adsorbent that was not modified chemically, using batch adsorption method, it was found that the percentage removal of lead and cadmium were: 99.4% and 88.4%, correspondingly at the doses of 3g and 3.5g. Similarly, [29] studied the removal of heavy metals using corncob as an adsorbent and discovered that the maximum removal of lead and cadmium from the synthetic wastewater were 100% and 85%, respectively, at the initial metal ion concentrations of 20 mg/L, adsorbent dosage of 5 g/L and contact time of 6 hours. The findings further suggest the potentials of corncob as an adsorbent.

Moreover, [30] produced an activated carbon from Corncob and used it to remove dye from sewage. The study established the adsorption capacity and removal efficiency of the corncob activated carbon to be 523.18 mg/g and of 99.52%, respectively for methylene blue. This also suggest the suitability of corncob activated carbon for the removal of dye from wastewater, which further affirmed its wide range of applicability in terms of pollutants removal.

Similarly, [28] treated synthetic grey wastewater using corncob as adsorbent. The study found the BOD and COD to be reduced to 65.9 mg/L and 228 mg/L, correspondingly from the initial concentrations of 367.9 mg/L and 472 mg/L. Conversely, the Total Dissolved Solids (TDS) increased from 512 mg/L to 600 mg/L. This observation of the increased in the TDS is in agreement with what is obtained in this study.

Furthermore, [4] carried out study on the assessment a rice husk adsorbent chemically modified with sodium hydroxide for the treatment of oil seed industrial effluent using batch adsorption method. The study reported the reduction of turbidity, BOD and COD by 81.46%, 25% and 85%, congruently, suggesting the suitability of rice husk, being an agricultural by product, in the treatment oil seed effluent. This indicates the need to explore more agricultural wastes that are readily available for applications as adsorbent the treatment of industrial effluent before the eventual discharge into the receiving streams. The Table 3 shows the comparisons of the various adsorbent materials in relations to the adsorbed materials.

4. CONCLUSION

The treatment of oilseed industrial effluent using corncob adsorbent, chemically modified with sodiumhydroxide was successfully carried out. The study revealed that the BOD, COD, lead and cadmium concentrations were droppedto 18, 3000, 0.075 and 0.047 mg/L, respectively, from the initial concentrations of 40, 7000, 1.268 and 0.138 mg/L, signifying the percentage reductions by 55.00%, 57.14%, 94.09% and 65.94%, respectively; with comparative adsorption capacities of 0.2978, 54.140, 0.0165 and 0.0012 mg/g at the contact time of 6 hours. Furthermore, the hydroxyl (OH) functional group that arose by virtue of impregnation of the corncob with 1M NaOH, resulted to a reduction in pH value of the oilseed effluent to increase from 4.80 to 7.52, which is acceptable for the discharge of industrial effluent into the receiving stream. This suggest the suitability of the modified corncob adsorbent in the removal of physical and chemical pollutants from oilseed industrial effluent. It is recommended that further studies should be carried out considering higher weight of the corncob adsorbent as well as upper contact time so that some of the pollutants considered in this work could fall within the recommended limit for discharge into receiving water.

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CREDIT AUTHOR STATEMENT

Yushau Muhammad Salis: Conceptualization, Investigation, Formal analysis, Data curation and Visualization. **Aliyu Adamu Dandajeh**: Supervision, Methodology, Writing-Original draft preparation, Writing-Reviewing and Editing.

DECLARATIONS

Conflict of interest 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.

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