

Modified corn cob adsorbent for heavy metal removal from wastewater

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Paper History

Received: 15th Jan, 2024

Accepted: 27th March, 2024

Published: March, 2024

Abstract:

A common agricultural waste, corn cob, has drawn interest as a possible adsorbent for the removal of contaminants from wastewater. Its effectiveness for removing heavy metals has been thoroughly investigated; however, its efficiency for nickel (Ni) has not been well explored. The purpose of this study is to study corn cob's potential as an adsorbent for removing nickel from wastewater. The corn cob was subjected to various pre-treatment methods, to enhance its adsorption capacity. The adsorption experiments were conducted under different pH levels (2, 4, 6, 8, 10, 12, 14), contact times (20, 40, 60, 80, 100, 120), and adsorbent dosage (0.05, 0.1, 0.15, 0.2 and 0.25) to determine the optimum condition for Ni removal. The adsorption capacity of corn cob was evaluated using adsorption isotherm and kinetics models. The results reveal that the highest Ni removal efficiency, with an adsorption capacity of 80% -86% was obtained at factor levels of: pH level of 6, contact time of 120 minutes and adsorbent dosage of 0.15. The adsorption process followed the Langmuir isotherm and pseudo-second-order kinetic model, suggesting a monolayer adsorption mechanism. Moreover, the pH, contact time and concentration significantly influenced the Ni removal performance. Overall, maize cob shows potential as an effective and low-cost adsorbent for Ni removal from wastewater, opening up options for sustainable wastewater treatment and resource recovery.

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Keywords: Heavy metals, Wastewater, Agricultural waste, Contaminants

1. Introduction

Environmental elements such as water and their sustainability are critical to the existence of the planet and all living creatures [1]. Any deterioration in one part of the system eventually affects the entire system since every creature in the ecosystem is linked by a life link [2]. Water is distinct from other environmental elements since it is necessary for life and cannot be substituted. In recent years, human concerns over water quality and quantity have grown [3]. Globalization of the industrial sector, the growth of urban and suburban areas, and agricultural areas that generate large amounts of wastewater are all threats to aquatic life [4].

An unsuitable substance typically a chemical or microorganism can contaminate a stream, river, lake, ocean, aquifer, or other body of water, leading to its loss in quality and endangering human health as well as the environment. But only 1% of the planet's freshwater is accessible to humans because of the limited water supply. It is stated that if nothing is done, the problems will only get worse by 2050, when groundwater consumption is expected to increase by one-third compared to current levels [5]. Overall, the importance of more advanced and efficient wastewater treatment techniques has been spurred by the need to protect the environment and the

public's health while also providing dependable and treatment solutions for wastewater [6].

Adsorption is a useful method for treating wastewater because it uses solid materials to draw contaminants out of liquid or gas. Numerous benefits come with this technology: it is highly effective at eliminating various pollutants; it can treat a wide range of wastewater types; it is more affordable than alternative methods; it can regenerate and reuse adsorbents; and it is easy to use and integrate with existing systems. Adsorption is a feasible and simple process to use in wastewater treatment when compared to other alternatives [6].

Activated carbon (AC) has been the most widely used adsorbent in the industries for treating liquids and gasses. Charcoal is the oldest known adsorbent for treating wastewater [7]. The process of making AC involves dehydrating the raw materials, carbonizing them, and then activating them. The resultant product is more porous and has a surface area of between 600 and 2000 m²/g [8]. Any low-cost material with high carbon content and few inorganic precursors, such as coal, wood, coconut shells, corn cobs, almond shells, peach stones, grape seeds, apricot stones, cherry stones, olive stones, peanut hulls, nut shells, rice husks, oil palm shells, and sugar cane bagasse, can be used to make industrial activated carbon

(AC), according to Jamaludin [9]. Other materials that can be used include; Groundnut shells, Palm Kernel shells, Coconut shells, bamboo, wood chips, corn cob, seeds, and sawdust [11], *canariumscheveinfurthii* nutshell [10], palm shell, rattan, mango stem peel, and corn cob [7].

In chemical activation, the precursor is treated with a chemical agent prior to being pyrolyzed at a lower temperature (between 400 and 6000°C) in the absence of air. Chemical activation has several advantages over heat activation. It produces a superior porosity structure by combining activation and carbonization in a single phase at lower temperatures [10]. The 1980s saw a sharp rise in the number of corn plantations, which was accompanied by a notable rise in the amount of agricultural waste (corn cob) produced in fields and industries [12]. Thus, corn cob is readily available. It was reported that, for every 100kg of corn grain, approximately 18kg of corn cob is produced [13]. According to Yusuf *et al.*, [8], manufacturing of AC with high specific surface area and pore size depends on the nature of the raw materials utilized as well as the procedures and environmental factors. Previous studies have demonstrated that high-grade AC can be made using locally available resources, and the result might be competitive with commercial AC.

Agricultural wastes like corncobs, *Canariumscheveinfurthii* nutshells, coconut shells, palm kernel shells, and macadamia nuts have all been studied by previous researchers [7, 14, 15]. Contamination of water by heavy metallic elements present in large quantities remains an intractable environmental menace. In recent times, increase in population led to intensified industrial activities resulting to more discharge of harmful and non-biodegradable heavy metal ions. Thus, the need for continuous efforts to treat industrial wastewater using waste and low-cost of agricultural based adsorbents cannot be over emphasized [2]. This research is aimed at synthesizing, characterizing and applying corn cob based adsorbent for the removal of Nickel contaminant from simulated wastewater.

2. Methodology

2.1 Sample material size and collection

One hundred (100) *Zea mays* cobs were collected in markets along Tanke-Unilorin road in strong polythene bags and transported to the laboratory for storage and research.

2.2 Preparation of corn cob adsorbent

To get rid of as many pollutants as possible, hydrochloric acid 0.1M was used to wash the corn cobs. The corn cobs were then extensively washed in distilled water to bring the material's pH level back to 7.0. It was then crushed after drying to constant weight. It was then packaged in an airtight polythene bag to protect it from moisture for later usage. The dried maize cob was soaked in an APA and distilled water solution to saturation. The impregnated corn cob was then dried for three hours at a temperature of 110 °C in an oven. Later, it was then dried in a muffle furnace at a temperature of 300°C for 2 hours. The activated corn cob was then washed thoroughly with

distilled water to remove any impurities or leftover chemicals. Then dried again to constant weight to remove any remaining moisture and after, stored in a desiccators.

2.3 Preparation of Ni(II) solutions

A stock solution of 1000 mg/L of Ni (II) was prepared by dissolving NiSO₄.6H₂O in deionized water. Other concentrations varying between 20 and 120mg/L were prepared from the stock solution by serial dilution.

2.4 Moisture Content

A given quantity of each sample of activated carbon was heated in a furnace at a temperature of 105°C for an hour until a constant weight was achieved. The ratio of change in weight to the original weight expressed in percentage gives the moisture content, MC. This is given in equation 1:

$$MC = \frac{WL}{WO} \quad (1)$$

Where WL = Weight loss (Original weight – final weight) and WO = Original weight

2.5 Product characterization

The activated carbon of the corn cob was characterised using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM-EDS) and Branueur–Emmett–Teller (BET) analyses.

2.6 Fourier Transform Infrared Spectroscopy

The Fourier Transform Infrared (FTIR) characterization of the corn (*Zea mays*) cobs and activated carbon was conducted to ascertain the possible changes on the functional groups on the surface of these materials because of the chemical activation and carbonization process.

2.7 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) was used on the biomass samples to analyze the cavities, granular pores and rough surfaces of carbon materials. Granular pores and cavities increase surface area of biochar. SEM micrograph was used to analyse the surface morphology of the corn (*Zea mays*) peels and the biochar.

2.8 Branueur–Emmett–Teller (BET)

Branueur-Emmett-Teller (BET) analysis gives precise evaluation on specific surface area and pore size distribution of materials. Prior to analysis, the samples were preconditioned to remove physically bonded impurities from the surface of the powder in a process called degassing or outgassing. This was accompanied by applying elevated temperature to the sample in a vacuum. This process was carefully controlled and monitored to generate the most accurate and repeatable results.

The surface area of the material was then determined by the physical adsorption of a nitrogen gas onto the surface of the sample at cryogenic temperatures. The amount of adsorbed gas was measured by volumetric technique. Evaluation of the BET surface area was done in

the linear region of the BET plot, which was systemically evaluated using the Rouquerol transform.

3. Result and discussion

The results obtained in this work with detailed discussion are presented in this section.

3.1 Moisture Content

The moisture content of the bio-adsorbent was determined using equation 1. It was calculated to be 2.6612g

3.2 Biochar Composition

The inorganic elements present in the biochar samples with their respective weight concentrations as analysed by EDS are presented in Table 1

Table 1: Biochar Composition

Element symbol	Element	Atomic concentration	Weight concentration
O	Oxygen	69.73	75.42
C	Carbon	30.27	24.58

3.3 Functional Group Analysis

The presence of functional groups was studied by FTIR as revealed in Figure 1. The increase in wavelength

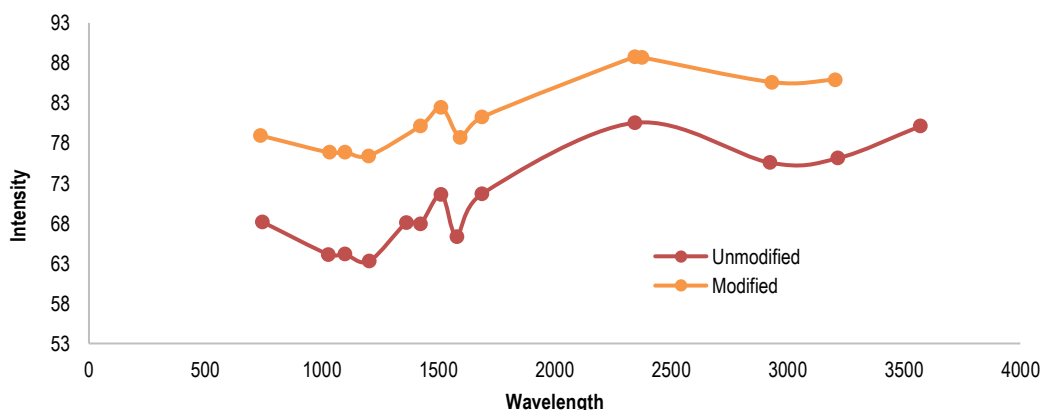


Figure 1: FTIR chart for modified and unmodified biochar

3.4 Bet analysis

The results of the Branueur–Emmett–Teller (BET) analysis of the biochar produced and is summarised in Table 4. The knowledge of the pore size distributions and adsorption isotherms helps to know the porous characteristics of the chars produced and their potential performance in adsorptive systems [19].

The pore volumes coupled with the specific surface area are important factors that determine the performance of the biochar as an adsorbent for the removal of pollutants from aqueous media [20]. The pore width mainly falls within the range of < 50 nm and >2 nm. This indicates that mesopores are mainly present, together with varying sizes of micropore and macropores.

The surface of the modified biochar is seen to be rough, not homogeneous, leaving interspatial spaces within (Figure 2). The biochar is also seen to have honeycomb

from 1688-2344 in both modified and unmodified adsorbents may be due to instrumental noise or impurities. In comparing the data for modified and unmodified, the appearance of new peaks at 1595.30, 2374.314, indicates changes in the chemical structure of the adsorbent's organic components. The new peaks produced the FTIR spectrum profile for a good water treatment process. The presence of Cl in the halo compound makes the material suitable for water purification [16]. The FTIR Spectra of both modified and unmodified adsorbent exhibit common functional group related to cellulose, lignin and organic components. The persistence of key function groups such as C-O and C-H vibrations indicates that the adsorbent's retains its organic character even after modification.

The presence of polar groups such as alcohol (OH), esters, ketones, aldehydes, carboxylic, ether and phenols suggest that the biochar samples have the potential to be used as adsorbent for aqueous pollutants [17] and as soil amendment for improving cation exchange [18]. These important functional groups are present because the thermo chemical conversion was a low temperature (300 °C) and char-optimised.

The functional groups observed in unmodified and modified corn hob are shown in Tables 2 and 3 respectively.

pores indicative of it being a suitable adsorbent for water purification and wastewater treatment. This is because of the pores filled with the acid. Rough surfaces increase porous characteristics and hence increase the adsorptive potential of the biochar. These features could provide adequate surface area for catalytic adsorption, heavy metal sequestration, reduces soil emissions of greenhouse gases, reduces irrigation, reduces nutrient leaching, nutrient retention (soluble organic and inorganic) and water holding capacity when incorporated in soil [21].

3.5 Effect of Adsorbent Dosage

The removal rate of nickel is increased significantly by increasing the adsorbent dose to 0.05g with further slight increase in nickel removal rate from 0.05g to 0.15 g and then remains relatively constant.

Table 2: Functional groups present in unmodified corn cob.

Wavelength	Functional group	Compound present
745	=C-H indicates out of plane bending mode =C-H stretching C-Cl stretching	Aromatic ring
1028 – 1203	C-O stretching C-O stretching C-F stretching C=O bending	Alcohol, Ether.
1364 – 1423	C-O-H bending -NO ₂ stretching	Aliphatic nitro
1513-1580	C=C stretching N-H bending N-H bending -NO ₂ stretching	Aromatic ring, amines, aromatic nitro
1688	C=O stretching C=O stretching C=O stretching C=O stretching	Aldehyde, phenyl, ketone.
2344 – 3216; 3570	C-H stretching O-H stretching (carboxylic acid) N-H stretching mode	Carboxylic acid, secondary amine

Table 3: Functional groups present in modified corn cob.

Wavelength	Functional group	Compound present
738	=C-H bending C-Cl	Aromatic ring
1032 – 1200	C-O stretching C-F stretching C=O bending	Alcohol, Ether
1423	C-O-H bending	
1513 – 1595	C=C stretching N-H bending NO ₂ stretching	Aromatic ring, secondary amine, aromatic nitro, aliphatic nitro, amide
1688	C=O stretching	Aldehyde, ketone, phenyl
2344 – 2374	C=N stretching	
2933	O-H stretching	Carboxylic acid
3205	O-H stretch N-H stretch	Carboxylic acid, primary amide, secondary amide.

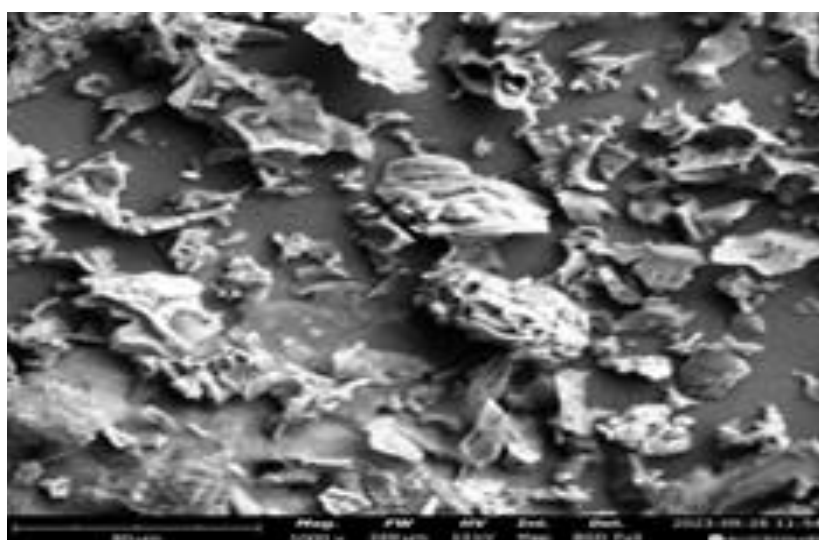


Figure 2: SEM image for modified corn cob

Table 4: Surface Morphology

BET surface area	245.484m ² /g
Pore volume	0.087cc/g
Pore width	5.839nm

Any additional addition of the adsorbent after this did not significantly alter adsorption, as seen in Figure 3. The description may be attributed to overlapping adsorption sites leading to overcrowding of adsorbent particles [22].

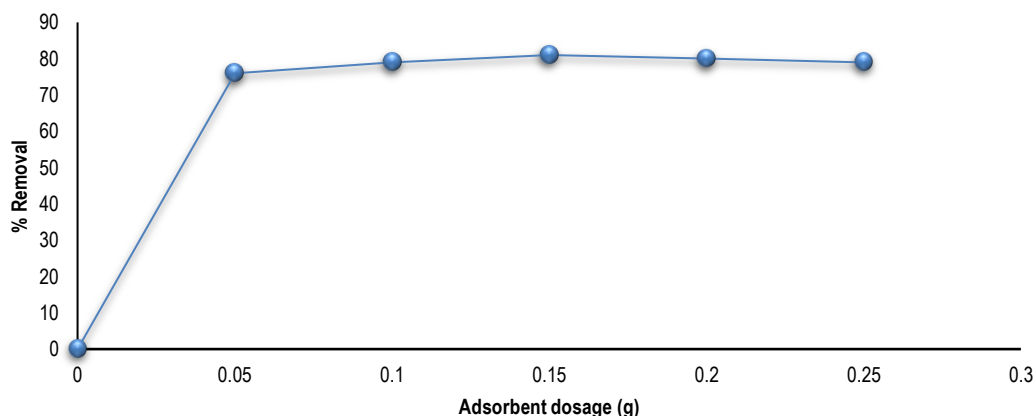


Figure 3: Effect of adsorbent dosage on Nickel removal from aqueous solution

3.6 Effect of Concentration

Figure 4 shows that at 20mg/l, there was rapid removal of nickel from solution. However, removal rate decreases with increase in concentration. This is as a result of competition for the available active sites at initial

concentration. As the initial concentration of nickel in solution increases, the available adsorption sites become occupied more rapidly. At higher concentration, the surface is already saturated leaving fewer active sites for adsorption.

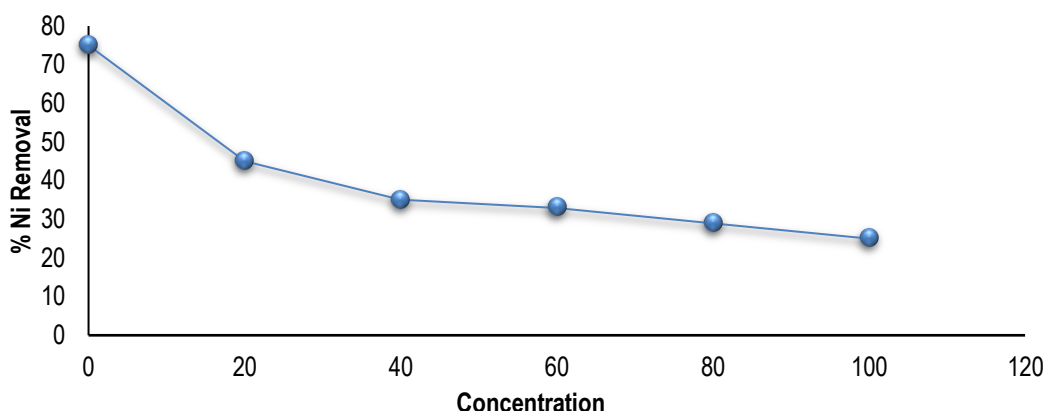


Figure 4: Effect of initial concentration on Nickel removal from aqueous solution

3.7 Effect of pH Solution

The surface charge of the adsorbent, the level of ionization, and the shape of the adsorbate are all defined by the pH value of the solution. In the adsorption of heavy metals, it therefore serves a crucial purpose [22]. Under acidic conditions, the adsorption of metal ions like nickel tends to increase. This is because the surface of the adsorbent often carries a positive charge at low pH. At high pH, the surfaces of the adsorbent become negatively charged. Maximum nickel removal was gotten at pH value of 6 as shown in Figure 5.

3.8 Effect of Contact Time

The effect of contact time on the elimination of Ni (II) by corncob powder adsorbent was depicted in Figure 6. 20 minutes of agitation resulted in the rapid removal rate of 80%. The graph demonstrates that Ni was rapidly adsorbed on the produced adsorbent in the first 20 minutes, and that Ni removal progressed gradually until it reached the highest removal rate of 87% at 120mins. The

pseudo-first-level and pseudo-second-level models (equations 2 and 3) are used to explain the adsorption kinetics among corncob adsorbent to extract nickel (II) among the many models that are often researched. In the equations, q_t is the maximum adsorption capacity (mg/g) at any given time t , q_e is the equilibrium adsorption capacity (mg/g), and k_2 is the second-order adsorption rate constant (g/mg*min). K_1 is the rate constant for the first-order equation (1/min).

$$\ln[q_e - q(t)] = -k_1 t + \ln q_e \quad (2)$$

$$q(t) = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (3)$$

When comparing the pseudo-first-order model (Figure 6) with the pseudo-second-order model (Figure 7), it was found that the pseudo-second-order model matched the sample and showed an outstanding correlation coefficient of 0.9964. The pseudo-first-order model could not explain these data because the mechanism was put into equilibrium within a short time.

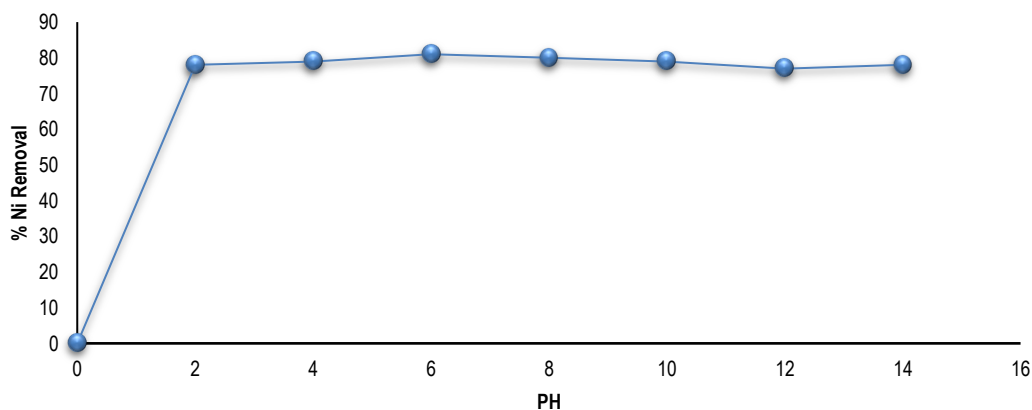


Figure 5: Effect of pH solution on Nickel removal from aqueous solution

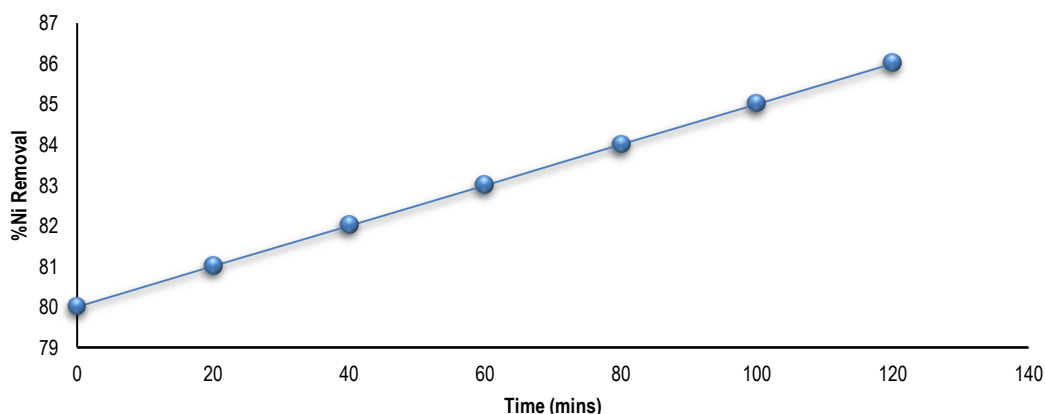


Figure 6: Effect of contact time on Nickel removal from aqueous solution

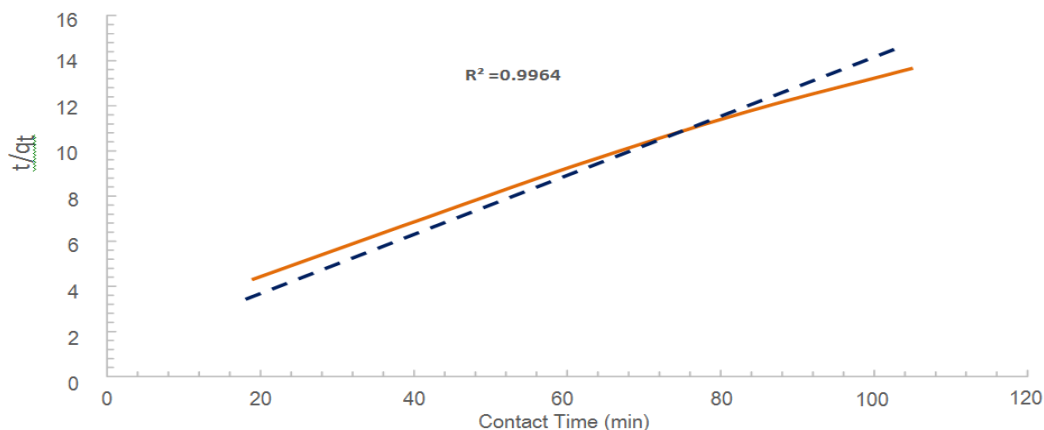


Figure 7: Pseudo-second-order kinetic plot for the removal of Ni (II)

3.9 Adsorption isotherm

Langmuir plot of the adsorbent for (Ni) removal at 25°C and Freundlich plot of the adsorbent for (Ni) removal at 25°C are shown in Figures 8 and 9 respectively. An adsorption isotherm, an equation that represents the connection between the amount of adsorbate adsorbed and the concentration of the adsorbent in the fluid phase, is the standard definition of an adsorption process. The interaction between the adsorbate and the adsorbent may be defined extremely effectively by the adsorption isotherm, making it crucial for design reasons [4]. By fitting experimental data to pre-existing adsorption isotherm models, the shape and degree of adsorption were

determined. Equations 4 and 5 represent the two most popular isotherm models, which were proposed by Langmuir and Freundlich respectively.

$$q_e = \frac{C_e q_L k_L}{1 + k_L} \quad (4)$$

$$q_e = K_F C_e^{1/n} \quad (5)$$

Where, q_L (mg/g) and q_e (mg/g) referred to saturated and equilibrium adsorption capacity, while K_L (L/mg) is constant obtain from Langmuir and K_F ((mg/g) (L/mg)^{1/n}), are constants obtained from Freundlich.

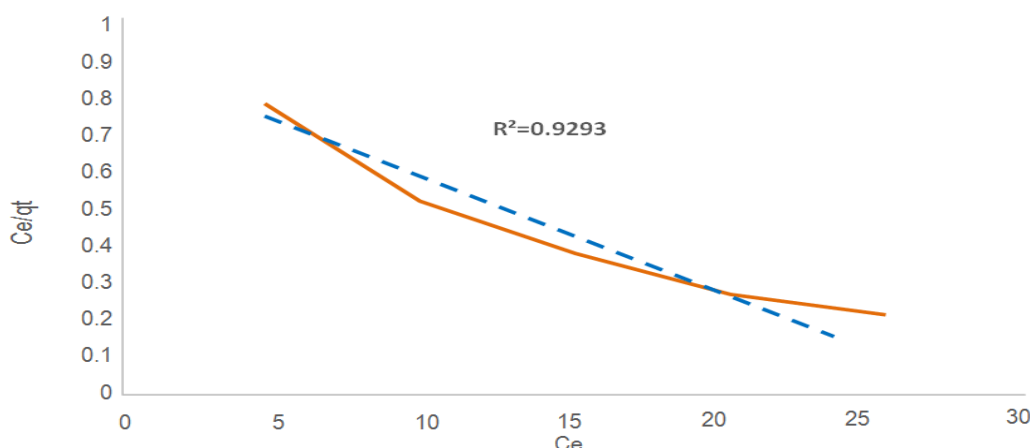


Figure 8: Langmuir plot of the adsorbent for (Ni) removal at 25°C

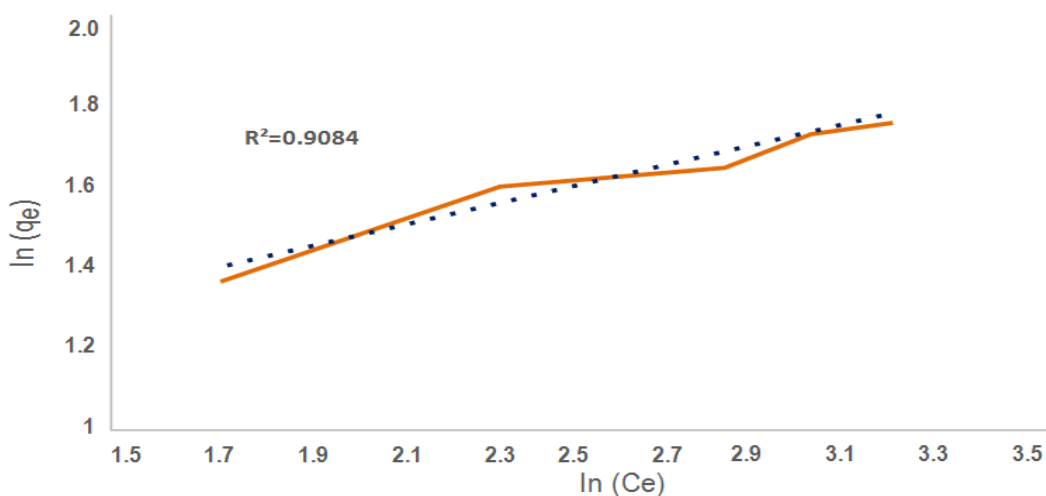


Figure 9: Freundlich plot of the adsorbent for (Ni) removal at 25°C

Since the regression coefficients (R^2) of Langmuir (0.92) are higher than the regression coefficients (R^2) of Freundlich (0.9084), it can be shown from a comparison of the Langmuir isotherm model and the Freundlich isotherm model that experimental data fits better with the Langmuir isotherm model. Other Scientists battling metal adsorption came to a similar conclusion [21]. While others took Freundlich's equations into account while calculating the adsorption [22].

4. Conclusion

The carbonization of the corn cob at 300°C for 2 hours, as well as the activation of the adsorbent with acid were pivotal in having effective active sites and mesopores needed for the adsorption process. Characterization of the prepared corn con adsorbent using SEM, BET, FTIR showed that the adsorbent exhibits promising characteristics, including surface functional groups such as carbonyl, hydroxyl for chemical interactions, a porous structure for enhanced surface area and a specific surface area conducive for adsorption. Adsorption tests using activated corn cobs showed high percentage removal of nickel in the range of 80-86% indicating that corn cob is a useful adsorbent in the treatment of wastewater.

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