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Removal of Cadmium, Nickel, and Zinc from Aqueous Solutions by Activated Carbon Prepared from Corncob - Waste Agricultural Materials

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Abstract

Adsorption of zinc (Zn^{2+}), cadmium (Cd^{2+}), and nickel (Ni^{2+}) from aqueous solutions by corncob (CC) and granular activated carbon prepared from corncob (GACC) were carried out. Synthetic solutions of Cd^{2+}, Ni^{2+}, and Zn^{2+} at 3.0 mg/L each were used to perform the adsorption process. A batch pattern was used to determine the removal efficiency of CC and GACC such as dose of adsorbents, contact time, and initial concentration of heavy metals, as well as kinetics studies and the adsorption isotherm parameters. The obtained results using either both the of CC and GACC separately were found to be matched with second-order model and the Langmuir isotherm model. Furthermore, the breakthrough study was conducted using CC, and GACC. The overall results in breakthrough curve indicated that adsorption of $Cd^{2+} > Ni^{2+>} Zn^{2+}$, and $Ni^{2+} > Zn^{2+} > Cd^{2+}$ on CC and GACC respectively. As demonstrated by R^2 and kinetic constant (k) values.

Keywords; Heavy metals; corncob; activated carbon; adsorption; water treatment; agricultural waste.

1. Introduction

It is well known that water is essential for all living creatures. It is essential for the consumption, personal hygiene, irrigation, farming, industrial sector, and other many sectors. The discharge of untreated or even partially treated wastewater is a threat to the environment and water resources [1,2]. It is extremely important to maintain the water quality standards set by applicable regulations and to eliminate hazardous substances from wastewater before discharging into the ecosystem [4]. Removal of heavy metals from wastewater is of utmost importance [4,6]. Heavy metals have long-term masking potential, highly toxic to man through the food chain. Consequently, removal of heavy metals from wastewater is essential [7]. Cadmium is released from various natural and anthropogenic sources to the atmosphere, aqueous and terrestrial environments. Cadmium is highly toxic to the kidneys. It can damages the kidneys' blood filtration system, resulting in the excretion of proteins in urine [4]. The severity of the effects depends on the duration and magnitude of exposure. Skeletal damage is another critical effect of long-term exposure to cadmium at high levels [8]. When it is breathed in, cadmium can cause lung cancer [9]. Metallic nickel is one of the lightest heavy metals. The process of using metals in equipment in industrial activities such as electroplating and alloys is the main source of nickel [4]. Sometimes nickel is found in groundwater as a result of dissolution from nickel-bearing rocks [10, 11]. Its prolonged contact with skin and mucous membranes can cause itching and sometimes produce allergies [12]. In general, contact dermatitis from skin exposure to nickel is the most common effect [13]. Also, ingestion of nickel salts can yield nausea, vomiting, and diarrhea, whereas chronic inhalation of nickel under the monoxide or metallic form can generate certain cases of asthma and tubular dysfunction [14]. Nickel organic compounds, such as tetra-carbonyl-nickel, are known to be very toxic and highly carcinogenic (lung cancer) [15].

Storing water in metals in tanks may contaminate it with zinc. Industrial sources of toxic waste sites may cause zinc in drinking water to reach levels that may cause health problems. The presence of large quantities of zinc in industrial wastewater could cause zinc-contaminated sludge to settle on the containers [16]. Also the intake of human being to a little amount of zinc can cause loss of appetite, decreased sense of taste and smell, slow wound healing, and skin sores

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[16]. There are several ways to remove zinc from water. The most important of which are ion exchange systems that can remove nearly 100% of zinc from water [18]. There is also a reverse osmosis method which effectively removes zinc from water by using semi-permeable membranes that prevent minerals from passing through it [16]. Water and wastewater handling has been studied by several treatment technologies including membrane filtration [17], chemical coagulation, electrochemical techniques [18,19], adsorption, and ion-exchange [18,19,20,21]. Other common and reliable techniques for wastewater treatment include constructed wetlands, up flow sludge blanket (UASB) and aeration are applied [22,23]. The adsorption technique is widely used in water treatment due to the high efficiency, low cost, simple in operation, and eco-friendly [23]. Physical adsorption is caused by the intermolecular force that exists between adsorbent and adsorbate. The force in physical adsorption is known as van der Waals force [21]. Since van der Waals force exists between any two molecules, physical adsorption can occur on any solid surface [22].

Chemisorption is a type of adsorption that involves a chemical reaction between the surface of the adsorbate and the adsorbent. Consequently, new chemical bonds are created on the surface of the adsorbent. The strong interaction between adsorbate and the surface of the substrate creates new types of electronic bonds; this includes the transfer, exchange, or sharing of electrons between adsorbents and adsorbate (atoms or molecules) to create a covalent or ionic bond. Thus, the chemisorption may not be completely reversible and may require high regeneration energy [22,24]. The molecules are adsorbed on the surface of the adsorbent through valence bonds to form a monolayer [21]. These properties facilitate possible to using AC in purification and pollutant removal from both liquid and gaseous media. The AC is also effective as catalysts and catalyst supports, widely applied to control air pollution and water purification. The disadvantage of activated carbon is due to its slow kinetics, being inert, bad selectivity and the interaction between carriers and active phase [25]. Treatment of wastewater by Ac that is made from solid agricultural waste is more economical because it is made from natural materials. Chemical activation is used with phosphoric acid and boric acid as an activation agent [26].

The CC contains organic carbon which acts as material support for microorganisms and is used as a carrier for heavy metals [27]. It is characterized by several chemical and physical properties that increase its efficiency in water treatment [28]. The CC consists of the following elements: C (24%), H (4%), S (1.4%). N (0.17%) [24]. To improve efficiency of the CC, it can be converted into activated carbon by chemical activation using concentrated phosphoric acid (H_3PO_4) [26]. Activated carbon prepared from corncob fulfills the quality requirements of the regular activated carbon [28]. This work aims to valorize a considerable agricultural solid waste residues namely Corncob (CC) via reuse in wastewater treatment. In the present study the CC was converted to granular activated carbon corncob (GACC) [18]. Both CC and GACC were used for the removal of Cd^{2+}, Ni^{2+}, and Zn^{2+} from artificial contaminated aqueous solution. The aim was extended to study the kinetic removal and isotherm of these metals.

2. Experimental

2.1 Preparation of AGCC

The CC waste is disposed of and incinerated to make activated carbon [28]. The CC was dried at 105℃ for 24 hours to reduce the moisture content, grounded manually, crushed with a mortar, separated by sieving at size ranged from 0.7 to 0.9 mm, then washed by distilled water (DW) many times, to remove color and dust [30].

The GACCs were prepared from corncob using phosphoric acid (H_3PO_4, 85.0 %) and boric acid (H_3BO_4, 99.5 %) as a chemical activating agent. The CC was added to the flask containing the activating agent. The pieces of CC are pre-carbonized then immersed in hydrochloric acid (HCl, 37.0 %), at 120 °C for 45 min, and then placed in an oven at 500°C for 1 h. The GACC obtained is washed several times using DW. After the pH of the solution reached neutral, the GACC was dried at the temperature of 105 ºC for 24 h [29,31].

2.2 Reagents

All chemicals used were high grade analytical reagents. The main chemical reagents used including phosphoric acid (H_3PO_4, 85.0%, Fischer scientific UK), potassium dichromate ($K_2Cr_2O_7$, 99.0 % Merck, Germany), boric acid (H_3BO_3, 99.5%, LOBA Chemie, India), hydrochloric acid (HCl, 37.0 %, Fischer scientific UK), nitric acid (HNO_3, 70.0%, Fischer scientific UK). The solutions were prepared using standard elements ($Cd(NO_3)_2$, $Ni(NO_3)_2$, and $Zn(NO_3)_2$), 1000 mg/L (Merck, Germany).

2.3 Instruments and characterization techniques

The following instruments were used through this study; muffle (Thermo Fisher Instrument, American provisioned of scientific), the atomic absorption spectrometer (AAS) equipped with graphite furnace to measure very low concentration (Thermo Fisher Scientific American provisioned of scientific), attached to a personal computer. Also, Drying oven

(Fisher Scientific Equipment, American provisioned of scientific), Digital electronic balance (PCE Instruments UK), and DW system (Millipore GER) were used. The pH measurements of the samples were achieved using pH-meter (AD110, Adwa, Hungary). Fourier-transform infrared spectroscopy (FTIR) analysis was performed using Thermo Fisher scientific (UK) for recording the spectra of adsorbents before and after treatment. Shaking was performed by Programmable shaker system (USA).

2.4 Batch studies using adsorbent

The studies focus on adsorption and desorption processes, in which kinetics and isotherms were comprehensively investigated. The effect of operating parameters towards adsorption efficiency of adsorbents such as adsorbent amount, contact time and initial concentration of metals, as well as breakthrough curve experiment, were examined.

When adsorbents were added into the solution containing Cd^{2+}, Ni^{2+}, and Zn^{2+}, the different effect of contact time, amount of adsorbent, and concentration of metals on removal efficiency (%), and capacity q_{max} (mg/g) of metals were measured [31]. The removal efficiency (R %), the amount of metals adsorbed on a specific amount of adsorbent q_e (mg/g) were calculated from the equations:

$$R\% = \frac{Co-Ce}{Co} \times 100 \qquad (1)$$

$$q_e\,(mg/g) = \frac{(Co-Ce)V}{m} \qquad (2)$$

Where R % is the removal efficiency, q_e is the amount of metals adsorbed on a specific amount of adsorbent (mg/g), C_0 is the initial concentration (mg/L), C_e is concentration after adsorption (mg/L), m is the dose of adsorbents (g), and V is the volume of solution (Liter).

2.4.1 Effect of adsorbent amount

The investigation of the effect of adsorbent dose on adsorption capacity of CC and GACC is also part of batch studies [32].

2.4.2 Effect of contact time

The effect of contact time on the adsorption efficiency of adsorbents is also comprehensively investigated by this study. This is because contact time is the most crucial parameter in batch studies.

2.4.3 Effect of initial concentration

The effect of a initial concentration of heavy metals on the adsorption efficiency of adsorbents are determined in this experiment; it was performed by preparing different concentrations of the heavy metals (2, 4, 6 ,8, and 10 mg/L) at the same time and dose.

2.4.4 Breakthrough curve experiments

Breakthrough in column tests can be defined as the amount of influent solution passing through the bed before a maximum effluent concentration is reached [33]. The inner diameter of column is 5 cm and length 50 cm, were packed with cotton as supporting material at 5 cm and adsorbents material with height of 15 cm, The heavy metals solutions with concentration of 3 mg/L were pumped up-ward through the column by flow rate of 2.5 mL/min. Sampling intervals were 0, 3. 6. 9. 12. 15. 18. 21. 24 h. The column was completely filled with 102 g of CC and 135 g of GACC. The breakthrough curve for the column was determined by plotting the ratio of the C_t/C_0 (C_t and C_0 are the heavy metals concentration of effluent and influent, respectively) against the time [33].

2.5 Isotherm models

The equilibrium between the concentration of heavy metals in solution and its concentration on the adsorbents resembles somewhat the equilibrium solubility of a gas in a liquid. These data are plotted as adsorption isotherms. The concentrations of remained heavy metals on the CC and GACC containing solutions are expressed as q (kg adsorbate (solute)/kg adsorbent (solid)), and in the concentration of heavy metals in fluid as C (kg adsorbate /m^3 fluid) [32]. Adsorption isotherm models such as the Langmuir and Freundlich were used in the adsorption of CC and GACC to determine the amount of adsorbate on the surface of the adsorbent [34].

2.5.1 Langmuir isotherm model

Langmuir isotherm model assumes monolayer sorption via physical forces. The Langmuir isotherm equation is given by

$$qe = \frac{C.K\,qmax}{1 + KL} \qquad (3)$$

and the linear form of this model is:

$$\frac{Ce}{qe} = \frac{1}{qmax}.KL + \frac{Ce}{qmax} \qquad (4)$$

Where q_{max} and K are the Langmuir constants, where q_e is the amount of metals adsorbed on specific amount of adsorbent (mg/g), C_e is the equilibrium concentration of the solution (mg/L) and q_{max} is the maximum amount of metals concentration required to form a monolayer (mg/g). The values of q_m and K can be determined from the linear plot of C_e/q_e versus C_e [30].

2.5.2 Freundlich isotherm model

Freundlich isotherms appear when the surface is heterogeneous and the absorption is multilayered and is bound to sites on the surface.

$$\log \mathrm{qe} = \log \mathrm{KF} + \frac{1}{\mathrm{n}} \log \mathrm{C}e \quad (5)$$

Where K is the Freundlich equilibrium constant (mg/g), 1/n = Intensity parameter C_e = Equilibrium concentration of adsorbate, q_e is the amount of solute adsorbed [11-13] [37].

2.6 Adsorption kinetics models

In the adsorption of CC and GACC, kinetic models can provide information to mechanisms of various factors such as the dose of adsorbents, contact time, and the initial concentration of the solution. Two kinetic models used to explain the mechanism of the adsorption processes, which are the pseudo-first-order model and second-order model. These models determine the relationship between change in concentrations of the Cd^{2+}, Ni^{2+}, and Zn^{2+} with increasing time (hour) [38].

2.6.1 The pseudo-first-order model

The non-linear equation of pseudo-first-order kinetic equation from the Lagergren equation is given by equation no. (6):

$$\log(qe - qt) = -\frac{k1}{2.303}\,.t + \log qe \qquad (6)$$

Where q and q_t are the amounts of adsorbed Cd^{2+}, Ni^{2+}, and Zn^{2+} (mg/g) at equilibrium and at any time t (h), respectively, and k is the rate constant of the first-order. The constants of the model can be calculated from the linear plots of log (q_e-q_t) vs. t [31].

2.6.2 The second-order model

Second-order follow adsorption mechanism, and the rate-limiting step may be chemisorption, involving valence forces or covalent forces between sorbent and adsorbate. The second-order reaction is calculated by equation 7:

$$\frac{t}{qt} = \frac{1}{k2qe2} + \frac{1}{qe}.t \qquad (7)$$

Where k is the rate constant of second-order sorption (g $mg^{-1}h^{-1}$) and q^2, k are the constants of the model were determined from plots t/q_t vs. t [31].

3. Results and discussion

Laboratory batch studies are useful in obtaining and providing fundamental equilibrium adsorption and kinetic data for the applied adsorbents. The importance of obtaining isotherms and kinetics curves lies in developing a model which accurately represents the results obtained and could be used for designing purposes. Moreover, the models applied to describe the breakthrough curve have a key role in the scaling-up procedure from laboratory experiments through pilot plant to industrial scale.

3.1 Characteristics of adsorbents

Figures (1, 2) show FTIR spectra of CC and GACC. The occurrence of the bands at 3300 cm^{-1} corresponds to O–H stretching vibrations that indicate the presence of hydroxyl groups, while that near 2844 cm^{-1} depicts C-H stretching that corresponds to the presence of alkanes [15]; the band at 2517.1 cm^{-1} corresponds to C=C bond [100]; the band at 1000 Cm^{-1} corresponds to C–O stretching, while that at 1517 and 600 Cm^{-1} showing characteristics of -N-O stretching and C–H bending, respectively [101]. These functional groups represent the chemically active components. The presence of the –OH group will initiate and accelerate the rate of condensation reactions created by dehydroxylation as a result of thermal decomposition of the cellulose content of the corncobs, while the C–H presence due to alkanes is connected to the reactions leading to hemicellulose degradation [101]. The existence of the C=C group, which is an indication of the presence of alkenes, facilitates reactions leading to lignin decomposition; while the group C–O, which is assigned to carboxylic groups in cellulose and hemicellulose [101].

Figures (1, 2) revealed that the bands at 3300 cm^{-1} and 1000 cm^{-1} in GACC higher than CC which is assigned to high density of oxygen atom in GACC groups (–OH group, and C–O stretching), that's refer to the chemically active components increased in GACC [15].

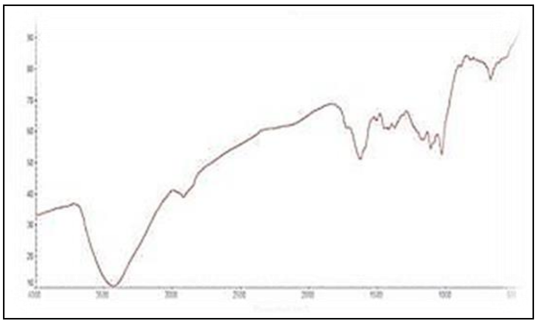

Fig 1: The FT-IR spectrum of the Raw CC

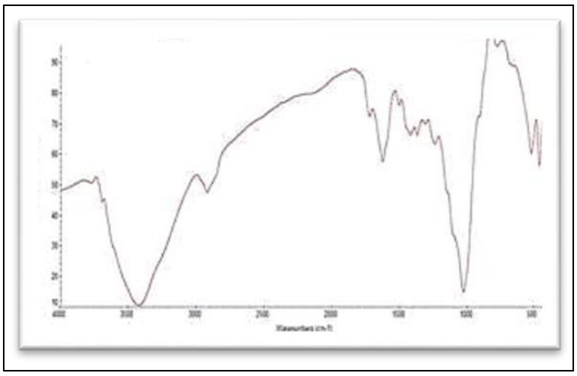

Fig 2: The FT-IR spectrum of the GACC

Adsorption isotherm indicates how adsorbate molecules distributed between the liquid phase and solid phase when adsorption process reaches an equilibrium state. Langmuir (Langmuir, 1915) and Freundlich (Freundlich, 1926) models were tested. The adsorbate molecules were tested for the removal of Cd^{2+}, Ni^{2+}, and Zn^{2+} from synthetic aqueous solutions. The effect of different doses of CC and GACC (0.1, 0.2, 0.5, 0.8, 1.0 1.2, 1.5, 1.8, and 2.0 g) on the adsorption of prementioned heavy metals. A linear plot of C_e/q_e versus C_e was obtained using CC and GACC, Table 1 and Figures 3 and 4.

3.2 Adsorption isotherms

Table 1: Freundlich and Langmuir isotherms for the adsorption of metals using CC and GACC

Metals	Adsorbent	Langmuir parameter			Freundlich parameter		
		R^2	q_m	K	R^2	N	K
Cd^{2+}	CC	0.974	0.21	3.7	0.147	8.7	0.29
Ni^{2+}		0.983	0.19	3.6	0.338	5.1	0.3
Zn^{2+}		0.970	0.08	1.3	0.205	7.2	0.185
Cd^{2+}	GACC	0.989	0.31	5.3	0.240	10	0.28
Ni^{2+}		0.991	0.27	13.9	0.220	10	0.32
Zn^{2+}		0.960	0.13	2.3	0.534	3.1	0.287

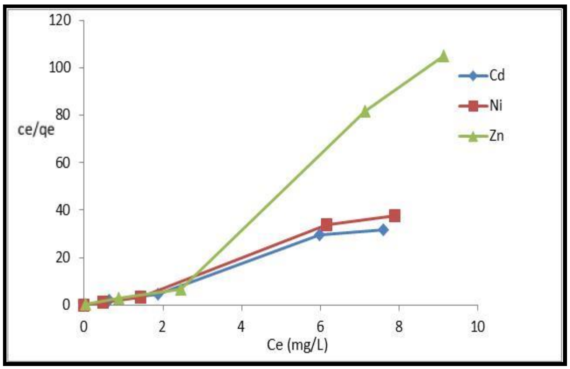

Fig 3: The Langmuir adsorption isotherm for Cd^{2+}, Ni^{2+} and Zn^{2+} using CC.

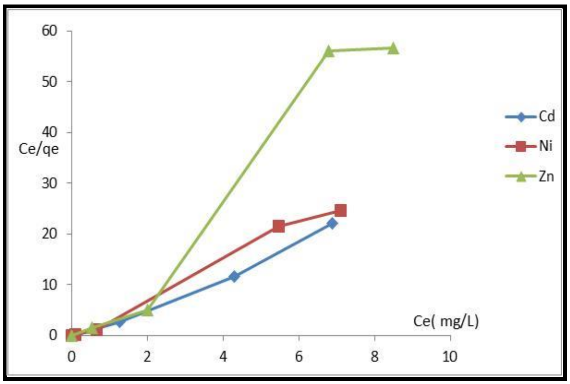

Fig 4: The Langmuir adsorption isotherm for Cd^{2+}, Ni^{2+}, and Zn^{2+} using GACC.

The data for the adsorption of metals onto CC and GACC were fitted to the Langmuir model, Table 1 and Fig (3.4). Taking into consideration the values of the correlation coefficient that gives better correlation were 0.974, 0.983, and 0.970, while in the case of GACC R^2 were 0.989, 0.991, and 0.960 for Cd^{2+}, Ni^{2+}, and Zn^{2+}, respectively. A better fit of the experimental data for the Langmuir equation explained the heterogeneity of the CC and GACC structure; so the strength of the bond created between the surface and the metal ions were not the same for all sites. As presented in Table 1, the Langmuir adsorption capacities (q_m) when using CC were estimated to be 0.21, 0.19, and 0.08 mg/g for Cd^{2+}, Ni^{2+} and Zn^{2+}, respectively. While the (q_m) at the use of GACC were 0.31, 0.27, and 0.13 mg/g for Cd^{2+}, Ni^{2+}, and Zn^{2+}, respectively. Values in the Langmuir isotherm indicated the monolayer adsorption capacity of the low-cost absorbent for heavy metals removal from the synthetic aqueous solutions [31].

Figures (5, 6) and Table (1) show the Freundlich adsorption isotherms with the correlation coefficient. The data for the adsorption of metals onto CC and GACC was non-fitted to the Freundlich model. R^2 = 0.147, 0.338, and 0.205 for Cd^{2+}, Ni^{2+}, and Zn^{2+}, respectively, at CC, while R^2 = 0.240, 0.220, and 0.534 using GACC for Cd^{2+}, Ni^{2+}, and Zn^{2+}, respectively.

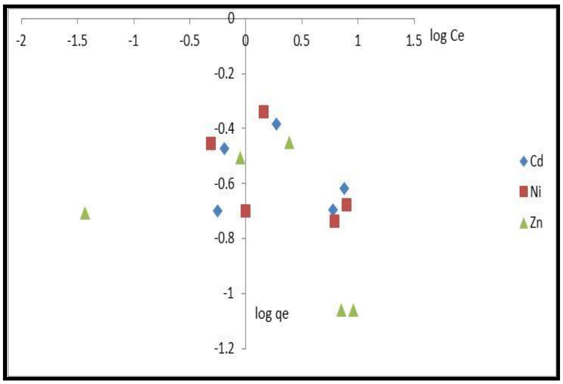

Fig 5: The Freundlich plot for adsorption of Cd^{2+}, Ni^{2+}, and Zn^{2+} onto CC.

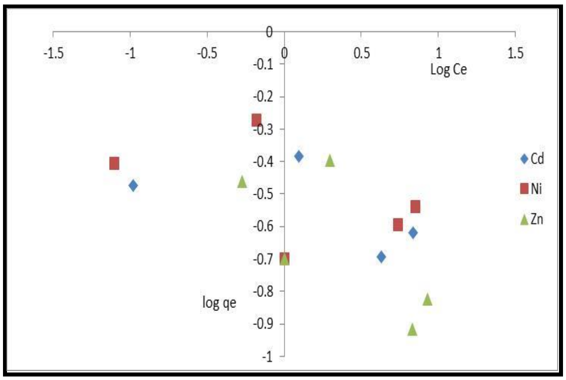

Fig 6: The Freundlich plot for adsorption of Cd^{2+}, Ni^{2+}, and Zn^{2+} onto GACC.

The magnitude of the exponent n in Freundlich isotherm gives an indication of the favourable nature of the sorption metals system. The n values (Table 1) obtained were 8.7, 5.1, and 7.2 for Cd^{2+}, Ni^{2+}, and Zn^{2+}, respectively, using CC, and 10.2, 10.1, and 3.1 for Cd^{2+}, Ni^{2+}, and Zn^{2+}, respectively, using GACC, which represents a range of beneficial adsorption between 1< n <10 for several investigated systems [31]. In this study, the values of n between 1 and 10 indicated the physical adsorption of metal ions onto the absorbent surface [41].

3.3. Kinetics studies

Adsorption of Cd^{2+}, Ni^{2+}, and Zn^{2+} was measured by pseudo-first-order and second-order kinetic equations. The first-order model described the sorption capacity of solids in solid-liquid systems, while the second-order model has been applied for the analysis of kinetics from liquid solutions [31]. The non-linear form of pseudo-first-order model is given in Figures 7 and 8, while the linear form of second-order model was shown in Figures 9 and 10 [31].

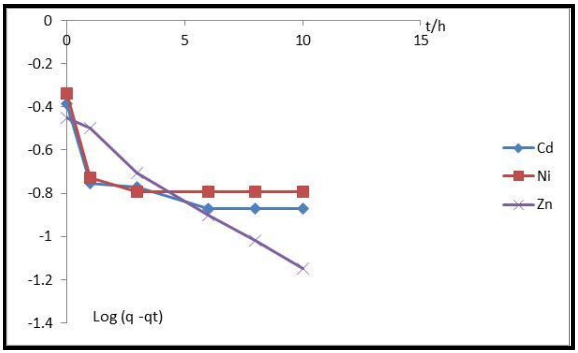

Fig 7: The pseudo-first-order kinetic models of Cd^{2+}, Ni^{2+}, and Zn^{2+} adsorption using CC.

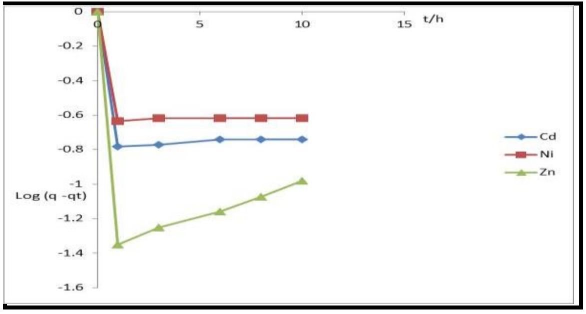

Fig 8: The pseudo-first-order kinetic models of Cd^{2+}, Ni^{2+}, and Zn^{2+} adsorption using GACC

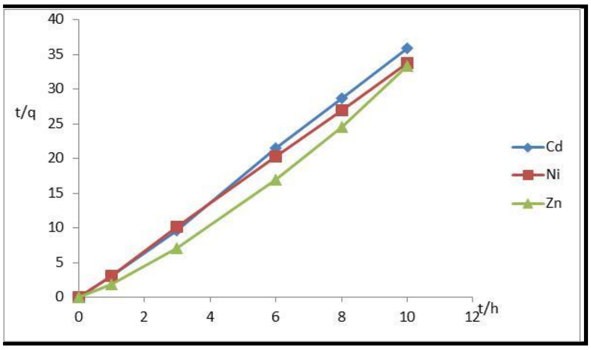

Fig 9: The second-order kinetic models of Cd^{2+}, Ni^{2+}, and Zn^{2+} adsorption of using CC.

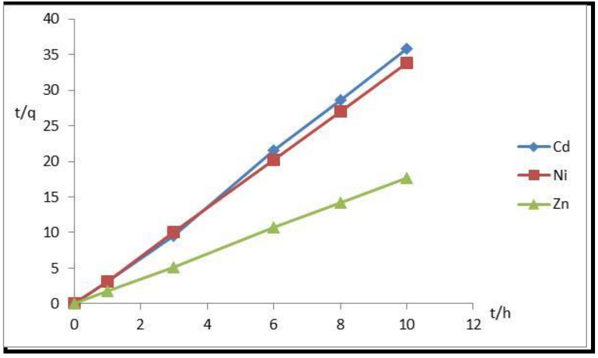

Fig 10: The second-order kinetic models of Cd^{2+}, Ni^{2+}, and Zn^{2+} adsorption using GACC.

Figures (7 -10) show a fit of the sorption kinetics of Cd^{2+}, Ni^{2+}, and Zn^{2+} at different time. The values of the rate constant and the correlation coefficient are listed in Table 2. The results indicated that the second-order kinetic model gave a good fit of the data for adsorption of Cd^{2+}, Ni^{2+}, and Zn^{2+} onto the CC and GACC. From the theoretical values of R^2 are very well in pseudo-second-order kinetic model. The adsorption of Cd^{2+}, Ni^{2+}, and Zn^{2+} on CC, and GACC follows the pseudo-second-order kinetic model, which relies on the assumption that chemisorption may be the rate-limiting step. In chemisorption, the metals ions stick to the adsorbent surface by forming a chemical bond and tend to find sites that maximize their coordination number with the surface [42].

Table 2: The kinetic adsorption of metals using CC and GACC

Metals	Adsorbent	Second-order parameter			First-order parameter		
		R^2	q_e	K	R^2	q_e	k
Cd^{2+}	CC	0.999	0.27	26.58	0.528	0.06	0.29
Ni^{2+}		0.999	0.29	105.99	0.272	0.02	0.40
Zn^{2+}		0.989	0.30	7.09	0.964	0.60	0.07
Cd^{2+}	GACC	0.999	0.27	26.58	0.283	0.069	0.27
Ni^{2+}		0.999	0.29	105.99	0.310	0.019	0.28
Zn^{2+}		0.989	0.30	7.09	0.114	0.60	0.04

3.4 Factors affecting on removal efficiency of adsorbents

3.4.1 Effect of contact time

Figures 11 and 12 depicts the effect of contact time for the metal ions' adsorption on CC and GACC surface. In the adsorption test, the rate of metal ions removal was relatively fast at the beginning due to the greater availability of the surface area. For both CC and GACC, the metal ions sorption shows a quick tendency to reach equilibrium. The maximum percent removal attained at the 6th h, after 6 h, the removal percentage remained relatively constant reaching 100 %. It was evident from Figures 11 and 12. This occurred due to a large number of vacant surface sites available for adsorption [43]. After the passing of time, the adsorbent surface becomes occupied, so it was difficult to adsorb other materials onto the surface but, when zinc is removed, the maximum removal percent was after 6 hours. But after 6 hours, the zinc is desorbed back into the solution due to the repulsive forces between the adsorbed molecules and the adsorbent surface [44].

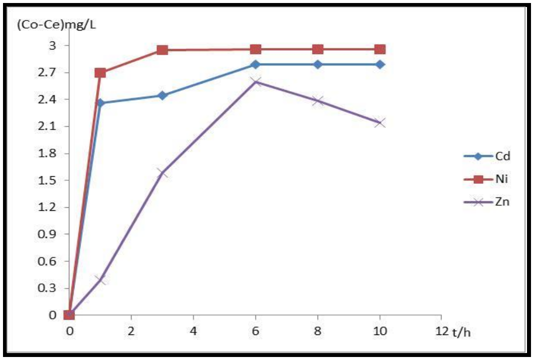

Fig 11: The effect of contact time on Cd^{2+}, Ni^{2+}, and Zn^{2+} adsorption using CC.

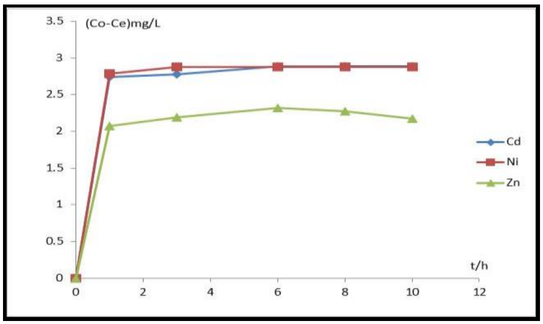

Fig 12: The effect of contact time on Cd^{2+}, Ni^{2+}, and Zn^{2+} adsorption using GACC.

3.4.2 Effect of adsorbent dose on percentage removal of heavy metals

The effect of the adsorbent dose on the removal of heavy metals (Cd^{2+}, Ni^{2+}, and Zn^{2+}) by CC and GACC is depicted in Figures (13, 14). The Cd^{2+}, Ni^{2+}, and Zn^{2+} removal using CC increased from 53.87 % to 100 %, 45.87 % to 100 %, and 55.55 % to 100 %, respectively, with increasing the amount of absorbent from 0.1 to 2.0 g. While Cd^{2+}, Ni^{2+}, and Zn^{2+} removal using GACC varied from 69.83 % to 100 %, 81.97 % to 100 %, and 51.22 % to 100 %, respectively, with increasing the amount of absorbent from 0.1 to 2.0 g. Increasing in removal percentage is due to an increase in the adsorbent surface area as well as the active sites available as the adsorbent is increased [44]. No increase in percentage removal beyond 1.0 g of adsorbent. This is associated with the saturation of adsorption sites [44].

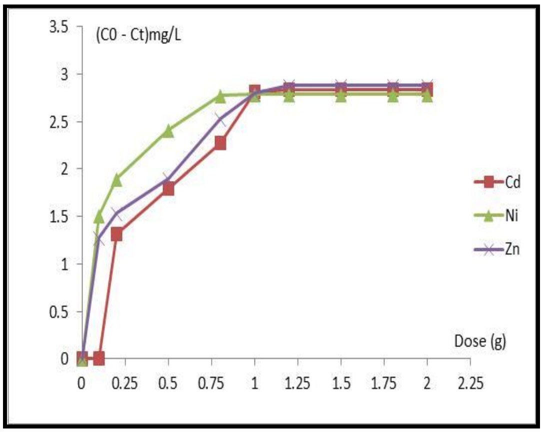

Fig 13: The effect of adsorbent dose on Cd^{2+}, Ni^{2+}, and Zn^{2+} adsorption using CC

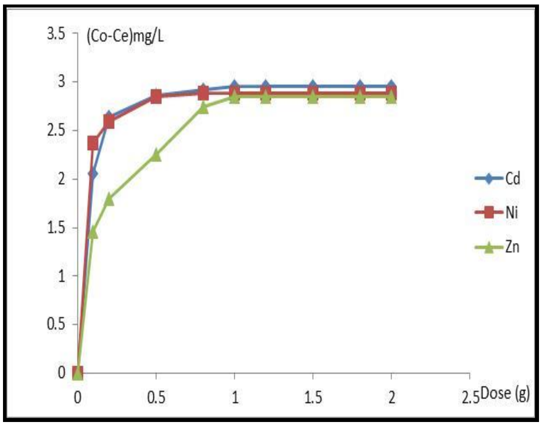

Fig 14: The effect of adsorbent dose on Cd^{2+}, Ni^{2+}, and Zn^{2+} adsorption using GACC

3.4.3 Effect of initial metal ion concentration

The amount of metal ions adsorbed by CC and GACC from aqueous solution was influenced by the initial concentrations of Cd^{2+}, Ni^{2+}, and Zn^{2+} in the synthetic aqueous solution. The initial concentrations of metal ions were 2, 4, 6, 8, and 10 mg/L while maintaining the adsorbent dosage at 1.0 g. Figures 15, 16 show the effect of initial concentration on the percentage removal of metal ions. The removal percentage of Cd^{2+}, Ni^{2+}, and Zn^{2+} decreased from 100 to 24 %, 100 to 21%, and 98.15 to 8.7% when adsorbate concentration changed from 2 to 10 mg/L, respectively, at a contact time of 6 h, and adsorption temperature of 25 ºC, at dose 1.0 g of CC. While at a dose of 1.0 g of GACC, the percentage removal of Cd^{2+}, Ni^{2+}, and Zn^{2+} decreased from 100 to 31.2 %, 100 to 28.9%, and 100 to 15% respectively, when adsorbate concentration changed from 2 to 10 mg/L at the same previously mentioned conditions. A decrease in percentage removal using CC and GACC adsorbent suggested that the amount of metal ions surpassed the fixed number of available active sites [44].

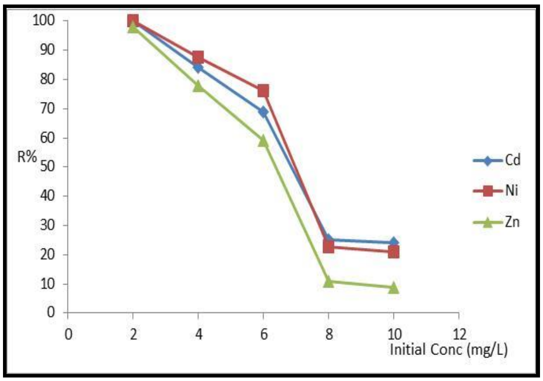

Fig 15: Effect of initial concentration of Cd^{2+}, Ni^{2+}, and Zn^{2+} on percentage removal using CC

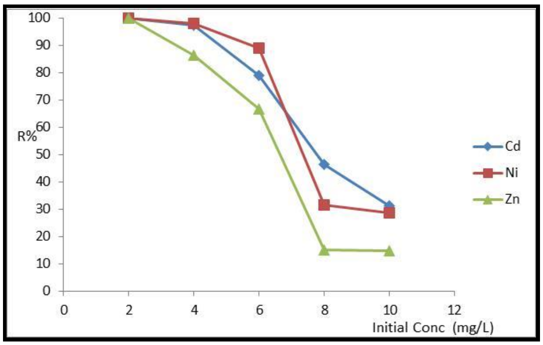

Fig 16: The effect of initial concentration of Cd^{2+}, Ni^{2+}, and Zn^{2+} on percentage removal using GACC

3.5. Continuous studies using CC and GACC

The CC and GACC columns were used to investigate there removal capacity of heavy metals under continuous flow conditions. This study can throw light on the data necessary for the optimization of the design experiments of adsorbents. Different contact times (3, 6, 9, 12, 15, 18, 21, and 24h) were examined to study the effect of the adsorptive capacity of CC and GACC. The rest of the other variables were kept constant. The concentrations of Cd^{2+}, Ni^{2+}, and Zn^{2+} in the synthetic aqueous solution were 3 mg/L each. The experiment for each system was carried out for 24 h. The operating conditions are given in Table 3. The removal efficiency (R %) of CC, and GACC for **Cd^{2+}, Ni^{2+}, and Zn^{2+}** at different flow contact times are shown in Figures 17 and 18 and Table 3. The removal efficiency of CC, and GACC reach to maximum at 12 h then the R% decrease with increase flow contact time due to The adsorption capacity of CC, and GACC were increased by increasing the time. The effect of flow contact time on the adsorption capacity showed that the adsorption of Cd^{2+}, Ni^{2+}, and Zn^{2+} ions on CC, and GACC. It was found that the adsorption of Cd^{2+}, Ni^{2+}, and Zn^{2+} ions on CC, and GACC was reversible when desorption was undertaken after 12 h [33],

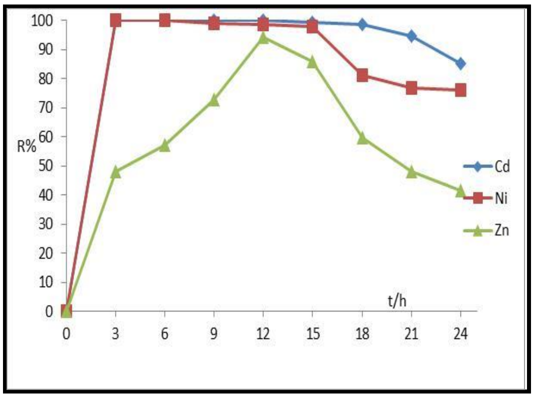

Fig 17: The breakthrough curves for Cd^{2+}, Ni^{2+}, and Zn^{2+} adsorption onto CC

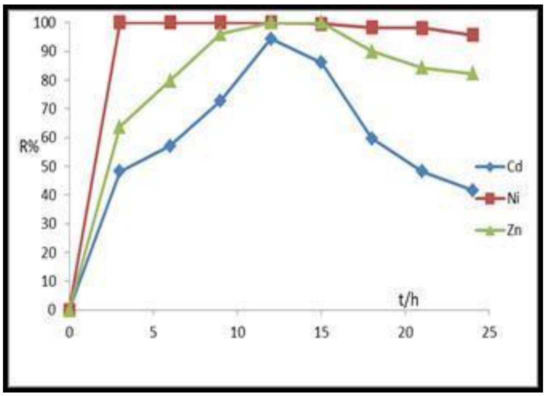

Fig 18: The breakthrough curves for Cd^{2+}, Ni^{2+}, and Zn^{2+} adsorption onto GACC

Table 3: The breakthrough data of corncob and activated carbon

Time (h)	Corncob (CC)			Granular activated carbon corncob (GACC)		
	R% of Cd	R% of Ni	R% of Zn	R% of Cd	R% of Ni	R% of Zn
3	100	100	48.24	48.24	100	63.69
6	100	100	57.01	57.01	100	79.79
9	100	99.07	72.80	72.80	100	96.06
12	100	98.81	94.29	94.29	100	100
15	99.47	97.89	85.96	85.96	99.50	100
18	98.69	81.18	59.64	59.64	98.21	90
21	94.71	76.75	48.24	48.24	98.10	84.24
24	85.36	76.01	41.66	41.66	95.61	82.19

4. Conclusions

Cadmium, nickel, and zinc are removed from synthetic aqueous solutions by CC and GACC. Consequently, both adsorbents can be used as effective and inexpensive materials in water and wastewater treatment. To increase the efficiency of the CC towards removing the heavy metals, it is converted into active carbon. The experimental data indicated that the adsorption process tends to follow the second-order kinetic model. Also, the removal efficiency of cadmium, nickel, and zinc using CC powder as an absorbent was found to be 100%, 100%, and 97.2%, respectively at an optimum dose of 1.0 g. The optimum contact time of both CC and GACC was 6 h. In addition, Langmuir isotherm was found to be the fitted model described the removal of the studied heavy metals.

Conflicts of interest

There are no conflicts to declare

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Reference

[1] H. I. Abdel-Shafy and M. A. El-Khateeb, 'E. Hunt, "Machine learning', *Egyptian Journal of Chemistry*, vol. 62, no. 12. pp. 2303–2312, 2019.

[2] H. I. Abdel-Shafy, M. A. El-Khateeb, and M. Shehata, 'Blackwater Treatment via Combination of Sedimentation Tank and Hybrid Wetlands for Unrestricted Reuse in Egypt', *Desalination and Water Treatment*, vol. 71, pp. 145–151, 2017.

[3] M. A. E.-K. Hussein. Abdel-Shafy, Madiha A. Shoeib and O. M. H. , Ahmed O. Youssef, 'Electrochemical treatment of industrial cooling tower blowdown water using magnesium-rod electrode', *Water Resources and Industry*, no. 1, 2020.

[4] E. Hunt, 'Machine learning: An artificial intelligence approach', *Mathematical Psychology*, vol. 27, no. 4, pp. 456–460, 1983.

[5] G. M, 'Water Purification by Membranes', *Journal of Polymer Science*, vol. 48. pp. 1685–1718, 2010.

[6] M. Jennifer, 'Conversion of Corn Cobs Waste into Activated Carbons for Adsorption of Heavy Metals from Minerals Processing Wastewater', *International Journal of Environmental Protection and Policy*, vol. 4, pp. 98–103, 2016.

[7] H. I. Abdel-Shafy and M. A. El-Khateeb, 'Heavy Metals in Citrus Fruits as Affected by Primary Treated Sewage Irrigation', *Egyptian Journal of Chemistry*, vol. 64, no. 1, pp. 165–176, 2021.

[8] Y. Luo, 'Study on the Repair of Heavy Metal Contaminated Soil', *IOP Conference Series: Earth and Environmental Science, China*, vol. 300, no. 3. 2019.

[9] Green Facts Scientific Board, 'Cadmium', *United Nations Environment Programme (UNEP)*, 2010. .

[10] D. James Huff, Ruth M. Lunn, Drph, Michael P. Waalkes, Lorenzo Tomatis, Peter F. Infante, Dds, 'Cadmium-induced Cancers in Animals and in Humans', *Innternational J ournal Occupation Environment Health*, vol. VOL 13, no. 2, pp. 203–212, 2007.

[11] Organization World Health, *Background document for development of WHO Guidelines for Drinking-water Quality. Nickel in Drinking-water*. 2007.

[12] S. E. Mohamed Lamine Sall, Abdou Karim Diagne Diaw, Diariatou Gningue-Sall and J.-J. Aaron, 'Toxic Heavy Metals: Impact on the Environment and Human Health, and Treatment with Conducting Organic Polymers, A review', *Environmental Science and Pollution Research*, vol. 27, pp. 29927–29942, 2020.

[13] J. J. Ahlström MG, Thyssen JP,Wennervaldt M, Menné T, 'A clinical review of immunology,epidemiology, exposure, and treatment.', *Contact Dermatitis*, vol. 81, pp. 227–241, 2019, doi: DOI: 10.1111/cod.13327.

[14] E. Denkhaus and K. Salnikow, 'Nickel Essentiality, Toxicity, and Carcinogenicity', *Critical Reviews in Oncology/Hematology*, vol. 42, no. 1. pp. 35–56, 2002.

[15] Samuel Buxton, 'Fact Sheet Nickel and Human Health: Nickel and Nickel Compounds Carcinogenity', *NiPERA*, no. December. pp. 1–8, 2018.

[16] B. M. J.K. Fawell, U. Lund, *Background document for development of WHO Guidelines for Drinking-water Quality. Zinc in Drinking-water*. 2003.

[17] H. H. Laura M, and Lothar Rink, 'The Essential Toxin: Impact of Zinc on Human Health', *International Journal of Environmental Research and Public Health*, vol. 7, pp. 1342–1365, 2010.

[18] J. Landaburu-Aguirre, E. Pongrácz, P. Perämäki, and R. L. Keiski, 'Micellar-Enhanced Ultrafiltration for the Removal of Cadmium and Zinc: Use of Response Surface Methodology to Improve Understanding of Process Performance and Optimisation', *Journal of Hazardous Materials*, vol. 180, no. 1–3. pp. 524–534, 2010.

[19] D. Ouyang, Y. Zhuo, L. Hu, Q. Zeng, Y. Hu, and Z. He, 'Research on the Adsorption Behavior of Heavy Metal Ions by Porous Material Prepared with Silicate Tailings', *Minerals*, vol. 9, no. 5. 2019.

[20] F. R. Laura Castro, J. Á. Muñoz, and Felisa González and María Luisa Blázquez, 'Batch and Continuous Chromate and Zinc Sorption from Electroplating Effluents Using Biogenic Iron Precipitates', *Minerals*, vol. 11, p. 349, 2020.

[21] M. Bratislava, 'Adsorption, Chemisorption, and Catalysis', *Chemical Papers 68*, vol. 68, no. 12, pp. 1625–1638, 2014.

[22] P. A. Webb, 'Introduction to Chemical Adsorption Analytical Techniques and their Applications to Catalysis', *MIC Technical Publications*, 2003.

[23] S. R. Farma, R. Fadilah, Awitdrus, N. K. Sari, E. Taer, 'Corncob Based Activated Carbon Preparation Using Microwave Assisted Potassium Hydroxide Activation for Sea Water Purification,The 8th International Conference on Theoretical and Applied Physics, Malaysia', 2017.

[24] T. Omotoso, 'Adsorption of Toxic Water Pollutants Using Modified Groundnut Shell', *The International Journal of Engineering and Science (IJES)*. pp. 2319–1805, 2017.

[25] A. L. and D. C. Dpto, 'Activated Carbon Fibers', in *Handbook of Advanced Ceramics*, Spain, 2013, pp. 156-169,2013.

[26] J. C. Hongyan Li, Pei Gao, Jianguo Cui, Feng Zhang, and Fang Wang, 'Preparation and Cr(VI) removal Rerformance of Corncob Activated Carbon', *Environmental Science and Pollution Research*, vol. 25, pp. 20743–20755, 2018.

[27] M. I. A. ELwahab, A. I. Hafez, F. M. Tera, K. I. E. -Nagar, W. S. I. A. EL-magd, and A. I. Hashem, 'Carbamated Corncobs As a Natural Coagulant for Water Treatment', *International*

Journal of Advanced Scientific and Technical Research, vol. 4, no. 8, pp. 74–84, 2018.

[28] M. Marlina, A. Putra, J. Hamka Air Tawar Padang, and I. Tel, 'Preparation and Characterization of Activated Carbon from Waste of Corn Cob (Zea mays)', *International Jaournal Of Scientific Research And Engineering Development*, vol. 2. pp. 221–227, 2019.

[29] L. Zhou, W. Xiong, and S. Liu, 'Preparation of a gold electrode modified with Au–TiO2 nanoparticles as an electrochemical sensor for the detection of mercury(II) ions', *Journal of Materials Science*, vol. 50, no. 2. pp. 769–776, 2014.

[30] L. Narayanan, 'Use of Corn Cob as Low Cost Adsorbent for the Removal of Nickel (II) From Aqueous Solution', *International Journal of Advanced Biotechnology and Research*. 2014.

[31] M. A. Mahmoud, 'Thermodynamics and Kinetics Studies of Mn (II) Removal from Aqueous Solution onto Powder Corn Cobs (PCC)', *Journal of Chromatography & Separation Techniques*, vol. 06, no. 07, 2015.

[32] K. N. I. Sadon, F. N., and Ahmmed Saadi Ibrahem, 'An Overview of Rice Husk Applications and Modification Techniques in Wastewater Treatment', *Journal of Purity, Utility Reaction and Environment*, vol. 1, no. 6, pp. 308–334, 2012.

[33] L. Bibiano-Cruz, J. Garfias, H. Llanos, and R. M. Javier Salas-Garcı, 'Batch and Column Test Analyses for Hardness Removal Using Natural and Homoionic Clinoptilolite: Breakthrough Experiments and Mmodeling', *Sustain. Water Resour. Manag*, vol. 2, pp. 183–197, 2016.

[34] A. M. Arquilada, C. J. Ilano, P. Pineda, and J. M. Felicita, 'Adsorption Studies of Heavy Metals and Dyes Using Corncob', *Global Scientific*, vol. 6, no. 12, pp. 343–376, 2018.

[35] P. M. Shruthi K, 'A Study on Utilization of Groundnut Shell as Biosorbent for Heavy Metals Removal', *International Journal of Engineering and Techniques*, vol. 4, no. 3, pp. 411–415, 2018.

[36] M. Ghasemi, N. Ghasemi, G. Zahedi, S. R. W. Alwi, M. Goodarzi, and H. Javadian, 'Kinetic and Equilibrium Study of Ni(II) Sorption from Aqueous Solutions onto Peganum Harmala-L', *International Journal of Environmental Science and Technology*, vol. 11, no. 7. pp. 1835–1844, 2014.

[37] I. Nhapi, 'Removal of Heavy Metals from Industrial Wastewater Using Rice Husks', *The Open Environmental Engineering Journal*, vol. 4, no. 1. pp. 170–180, 2011.

[38] D. Suteu, T. Malutan, and D. Bilba, 'Agricultural Waste Corncob as a Sorbent for Removing Reactive Dye Orange 16: Equilibrium and kinetic Study', *Cellulose Chemistry and Technology*, vol. 45, no. 5–6, pp. 413–420, 2011.

[39] A. T. Pelangi Eka Yuwita, Kusuma Wardhani, and. Sunaryono, 'Structural, Morphological, and Functional Group Analysis of Corncob Powder', 2020.

[40] A. Anukam, B. Goso, O. Okoh, and S. Mamphweli, 'Studies on Characterization of Corn Cob for Application in a Gasification Process for Energy Production', *Journal of Chemistry*, 2017.

[41] H. Kohl, R. Orth, O. Riebartsch, M. Galeitzke, and J. P. Cap, 'Support of Innovation Networks in Manufacturing Industries through Identification of Sustainable Collaboration Potential and Best-Practice Transfer', *Procedia CIRP*, vol. 26, pp. 185–189, 2015.

[42] K. K. P. Senthil, 'Eqilibrium and Kinetic study of Adsorption of Nickel from Aqueous Solution onto Bael Tree Leaf Power', *Engineering Science and Technology*, vol. 4, no. 4, pp. 351–363, 2009.

[43] K. Rifaqat, 'Kinetics and Isotherm Studies of Cd(II) Adsorption from Aqueous Solution Utilizing Seeds of Bottlebrush Plant', *Applyed Water Science*, vol. 4, no. 383–371, 2014.

[44] M. Daniel Muvengei, and Haron Mbuvi, 'Removal of Pb and Cd Ions, Colour and Turbidity from Water Using Carbon and Ash Derived From Maize Cobs', *Journal of Applied Chemistry*, vol. 10, no. 6, pp. 58–68, 2017.