

Effect of Chemical Treated Okra Waste for Heavy Metal Adsorption from Natural Gas Production Wastewater

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Abstract

Nowadays, one of the leading environmental pollutants is heavy metals. Hence, heavy metals in wastewater must be removed before discharge because they are toxic even at low concentrations. This research aims to evaluate the efficiency of okra waste as an adsorbent for heavy metals removal from wastewater in natural gas production. In this study, chemical activation of okra adsorbent was processed to increase the surface area of okra adsorbent for better adsorption, whenever the impregnation of the powdered okra waste was performed using phosphoric acid (H_3PO_4) as the impregnating agent. The okra powder was impregnated at a rate of 4: 1 (v / m). The FTIR was used to characterize the okra-activated carbon and the peaks showed the presence of functional groups such as Hydroxyl (OH), Amino (N-H), Carboxyl (C=O, C-O-C), C-O stretching and M-O at 3390.05, 2905.5, 1640-1658, 1050.05 and 650 stretching bands respectively. Furthermore, the batch adsorption experiments were conducted via varying agitation speed, contact time, adsorbent dose and adsorbent particle sizes. The results showed that the maximum removal percent of Cd^{2+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Ag^{2+} and Ba^{2+} metal ions had been observed to be at an agitation speed of 1000 rpm, contact time of 90 min, okra adsorbent dose of 0.25 g and particle size of 1.00mm. Indeed, the okra adsorbent showed a very high adsorption capacity for Cu^{2+} at 14.8 mg/g, followed by Pb^{2+} , Zn^{2+} and Cd^{2+} at 8.37 mg/g, 7.09 mg/g and 1.79 mg/g mg/g respectively and the R_L value in the present study for Cd^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+} ions were found to be 0.0003, 0.0027, 0.0001 and 0.0002 respectively. Therefore, all values of R_L were less than one, indicating that the adsorption of these heavy metal ions onto okra adsorbent was favorable. The experimental findings show that okra wastes from agricultural by-products may be a low-cost adsorbent for future research to remove additional heavy metals owing to their high effectiveness in removing Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} ions from wastewater.

Keywords: Heavy metals, Pollutants, Toxic, Agricultural by-products, Okra waste, Wastewater, Batch adsorption, Langmuir isotherm.

1. Introduction

Due to the rapid development of industry and the over-exploitation of natural resources in many countries, the levels of industrial pollution have been steadily rising [1]. The fast rise in water use owing to population expansion, urbanization, and industry is one of the most significant global concerns. As a result, industrial effluents pollute most water supplies, affecting ecosystem quality and

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the health of all living things [2]. For instance, industrial effluents including various organic and inorganic contaminants contribute considerably to freshwater reservoir pollution and depletion [3]. Heavy metals are among the most common pollutants in wastewater, and they are defined as metallic elements with a density of more than 6.0 g/cm³ when compared to water.

However, some heavy metals like Chromium (Cr), Cadmium (Cd), Mercury (Hg), Lead (Pb), Copper (II), Zinc (II) and Nickel (Ni) in their mixed or elemental forms, might be deemed harmful. Heavy metals are also highly soluble in aquatic settings, making them easily absorbed by biological organisms. As a result, heavy metals in wastewater that exceed permissible limits can negatively affect humans, other creatures, and the ecosystem [4]. Singha and Guleria (2015) reported that heavy metal ions are considered non-biodegradable and can accumulate in biological tissues, resulting in various illnesses and disorders. Notably, they must be removed before being discharged because they are toxic even at low concentrations. Therefore, their concentrations in drinking water, wastewater, and agricultural water must be minimal [5]. Table 1 summarizes some heavy metals, focusing on their major sources, health effects, and the permitted quantity in drinking water. Metals such as silver (Ag), iron (Fe), manganese (Mn), molybdenum (Mo), boron (B), calcium (Ca), antimony (Sb), cobalt (Co), and others are commonly found in wastewater and must be removed [6].

Heavy metals must be removed from wastewater using trustworthy technologies before it is discharged into the environment. Ion exchange, chemical precipitation, reverse osmosis, evaporation, membrane filtration, and adsorption on activated carbon and biological materials are among the most extensively used techniques for removing heavy metals from wastewater [7]. However, the method requires many chemicals to reduce the metal to an acceptable level for discharge and long-term environmental impacts. However, every technique has its advantages and disadvantages [8]. In general, most available processes have costly disadvantages. It is also difficult to use them on a wide-scale application. In addition, they are technically complex, can only be used for wastewater treatment in specific cases, and there is a massive quantity of toxic sludge that needs additional treatment [9]. Among all methods, adsorption is considered a suitable method because of its ease of use, and its simple operation and design [8]. Other advantages are the utilization of low-cost adsorbent materials and their efficiency in decreasing heavy metal ion concentrations to inadequate levels [10]. Adsorption can be defined as the accumulation of a substance at a surface or interface.

In wastewater treatment, the adsorption process occurs when a solid adsorbent and polluted wastewater come together. The pollutant being adsorbed is referred to as an adsorbate, and the adsorbing phase is referred to as an adsorbent [11]. However, adsorption efficiency is determined by the adsorbent's properties and several other factors such as pH, temperature, initial concentration, contact time, adsorbent amount, particle size of adsorbent, and others [10]. Normally, adsorption is particularly attractive when the adsorbent is inexpensive and does not require pre-treatment [12]. Agricultural by-products as adsorbents have recently encouraged much interest in studies for extracting heavy metals from industrial effluent [13]. Agricultural waste is one of the rich sources of low-cost adsorbents besides industrial by-products and natural materials. Due to its abundant availability, agricultural waste offers little economic value and creates serious disposal problems [6]. Heavy metals have been effectively removed from industrial wastewater using activated carbons from agricultural by-products [14]. Agricultural by-products have become increasingly popular as adsorbent materials to cleanse heavy metal-contaminated wastewater in the last decade since they are less costly, biodegradable, plentiful, and efficient [10].

Furthermore, using agricultural or fruit waste as a raw material by reusing solid waste lowers total costs and prevents surface water contamination [3]. Various waste products, including rice husk, wheat straw, wood waste biomass, sawdust, okra waste, wasted tea leaves, peanut husk, orange peels, and fruit debris, have been utilized to make biochar, which is used to remove metals or metalloids from polluted wastewater [15]. The functional groups like carboxyl, phenol, methyl and hydroxyl are the composition of agricultural wastes, which may be treated chemically and physically to increase the adsorption capacities to heavy metals [16]. These non-conventional adsorbents from agricultural waste

are predicted to be less effective (in terms of adsorption capacity) than the literature's super-adsorbents (complex materials such as modified chitosans, activated carbons, structurally complex inorganic composite materials, and so on), but their low cost makes them competitive [17]. Among these natural biomasses, cellulose okra fiber is one of the most promising biomasses for removing heavy metals from wastewater as an adsorbent. Okra fiber is mainly composed of cellulose, hemicellulose, and lignin and is agricultural waste biomass. Okra fibers are taken from the stem of a Malvaceae plant that originated in Egypt but is now farmed for nutritional purposes in tropical, subtropical, and warm temperate climates across the world [5].

Table 1. Typical heavy metals g in wastewater and their sources, their effects and the permitted amounts based on the World Health Organization (WHO) recommendations [6].

Common heavy metal	Main sources	Main organs and systems impacted	Permitted amounts (mg)
Lead (Pb)	Lead-based batteries, solder, alloys, cable sheathing pigments, rust inhibitors, ammunition, glazes and plastics stabilizers	Bones, liver, kidneys, brain, lungs, spleen, Immunological, hematological, cardiovascular and reproductive systems	10
Arsenic (As)	Electronics and glass production	Skin, lungs, brain, kidneys, metabolic system, and endocrine	10
Copper (Cu)	Corroded plumbing systems, electronic and cables industry	Liver, brain, kidneys, cornea, gastrointestinal, lung, immunological and haematological systems	200
Zinc (Zn)	Brass coating, rubber products, some cosmetics and aerosol deodorants	Stomach cramps, skin irritations, vomiting, nausea, anaemia and convulsions	300
Chromium (Cr)	Steel and pulp mills and tanneries	Skin, lungs, kidneys, liver, brain, pancreas, tastes, gastrointestinal system	50
Cadmium (Cd)	Batteries, paints, steel industry, plastic industries, metal refineries and corroded galvanized pipes	Bones, liver, kidneys, lungs, testes, brain, immunological system and cardiovascular system	3
Mercury (Hg)	Electrolytic chlorine and caustic soda production, runoff from landfills and agriculture, electrical appliances, industrial and control instruments, laboratory apparatus and refineries	Brain, lungs, kidneys, liver, immunological, cardiovascular, endocrine, and reproductive systems	6
Nickel (Ni)	Stainless steel and nickel alloy production	Lung, kidney, gastrointestinal distress, pulmonary fibrosis, and skin	70

The innovative, environmentally friendly, cost-effective, and locally accessible raw Okra waste derived from agricultural by-product sources was created and activated utilizing phosphoric acid as an activating agent in the current study. Furthermore, powdered okra has been employed as an adsorbent to remove heavy metals such as Cu^{2+} , Pb^{2+} , Cd^{2+} , and Zn^{2+} from wastewater in natural gas production sampled from Petroleum Temane SASOL plant located in Inhambane, south province of Mozambique. The batch method was then used, with various parameters such as contact time,

agitation speed, particle size of okra adsorbent material, and amount of okra adsorbent material being studied to obtain the maximum amount of heavy metals removed from wastewater, and the Langmuir isotherm model was used to describe the adsorption isotherm [18]. Table 1 shows and describes some heavy metals determined in wastewater from natural gas production using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), their effects on human health when exceeding the permissible limit and the permitted amounts based on World Health Organization (WHO) recommendations.

The study by Saka and Mas (2012) explained that the adsorptive removal of organic and inorganic substances from wastewater by biomass-derived activated carbons depends upon the surface area, the pore volume and the pore-size distribution carbons. However, the effectiveness of the adsorption relies not only on the characteristics of the adsorbent but also on different parameters, including pH, temperature, initial concentration, contact time, particle size of the adsorbent, etc. These parameters should also be considered while examining the potential of low-cost adsorbents [10]. The following paragraphs represent the most common and effective factors in the rate of the adsorption process.

(i) Effect of Solution pH

A previous study conducted by Hashem (2007) [32], explained that the pH value of the aqueous solution is an essential controlling parameter in the adsorption process of HM/ SD using either batch mode process or fixed-bed column. The research showed that the pH values affect the adsorbent surface charge, the degree of ionization, and the speciation of adsorbate during adsorption. In general, the adsorption of most metals on AC adsorbents increased with the increase in pH. This was attributed to the fact that the protonation of the active sites at low pH (< 4) at the carbon surface was enhanced. This refused the formation of links between cationic metals and protonated active sites. Some authors have reported that metal complexes form at higher pH and result in precipitation; therefore, the separation may not be due to adsorption.

(ii) Effect of Agitation Speed and Contact Time

Sulyman et al. (2017) explained the equilibrium time as a crucial element to study when considering an economic wastewater treatment application [35]. Simply put, there are three stages (phases) for the sorption process as follows: in the initial state, the sorption process is very rapid, and the rate of removal is higher because of the large amount of adsorbate attached to the sorbent within the first period time of adsorption. The higher sorption rate at the beginning can be attributed to the presence of a larger surface area represented by the adsorbent and the availability of free active sites at the beginning time for the adsorption of the adsorbate. After this period, as the contact time increases, the sorption rate gradually becomes relatively slower and, at some point in time, reaches a constant value where no more adsorbate is removed from the solution (transition phase). Finally, the process attains a plateau state (saturation phase). The lack of free active sites on the adsorbents at this time is the reason behind this behavior.

(iii) Effect of Adsorbent amount

On the other hand, when dealing with the batch mode technique, the amount of adsorbents (concentrations) is always and theoretically considered as a correspondent to the bed height factor. The percentage of adsorption increases with increases in adsorbent dosage, but the number of molecules adsorbed per unit mass of adsorbent decreases. As the number of adsorbents increases, the number of adsorption sites increases and thus increases the adsorbent surface area. The removal of heavy metals from aqueous solution on AC is also affected by the modified AC prepared from okra agricultural waste [35].

(iv) Effect of Particle Size

The particle sizes of adsorbent materials are an essential parameter in the adsorption process. For example, powder-activated carbon (PAC) is better than granular-activated carbon (GAC) in metal adsorption capacity due to its larger pores and faster adsorption rate. The larger pores of PAC allow by entrance the additional removal of these contaminants from their aqueous phase to take place; the authors also attributed the result to PAC's larger pores, permitting HMs to be more quickly adsorbed inside internal sites and thus wholly occupying these active sites. The adsorption capacity of contaminants decreases with increasing particle size. Hence, the percentage removal of contaminants also reduces when used with different natural materials as adsorbents for the adsorption of contaminants [35].

2. Methods

All chemical reagents used in this study were of analytical grades, purchased from suppliers of laboratory reagents in Maputo, Mozambique and used as received. These included deionized water, hydrogen peroxide (H_2O_2) and Nitric acid (HNO_3) used for wastewater sample extraction and phosphoric acid (H_3PO_4) used for activating powdered okra carbon. The batch adsorption experiments were all performed in Eduardo Mondlane University, chemical engineering and chemistry department laboratories.

2.1. Study design

Figure 1 describes briefly all procedures involved during this research, from the sample collection until the samples were analyzed through the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) Analytical instrument.

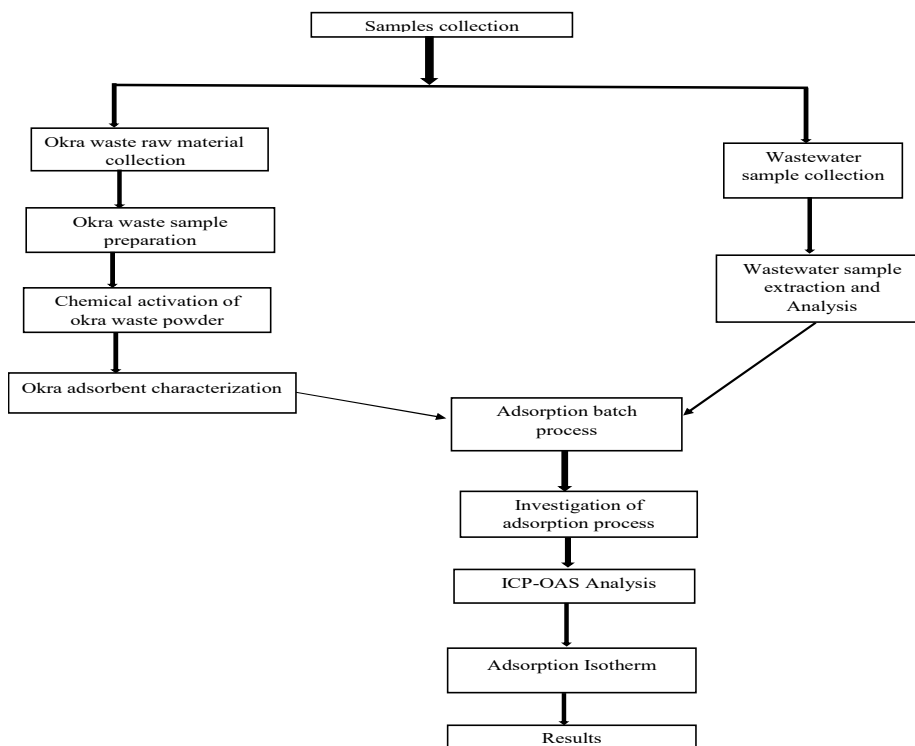


Figure 1. Experimental design of the study

2.2 Samples collection

The raw materials samples, such as okra waste and wastewater, were collected in Mozambique. The raw okra wastes from agricultural by-products were collected from okra plant farmers in Maputo, Mozambique and some agricultural food concern markets in Maputo city. Wastewater samples were collected from the Petroleum Temane SASOL plant located in Inhambane, the southern province of Mozambique.

2.3 Preparation of adsorbent from okra waste

The collected okra wastes from agricultural by-products were sorted and cleaned, and seeds were removed and cut into small pieces to facilitate drying. The pieces were dried for 6 hours at 110°C in an oven to eliminate moisture and other volatile contaminants [19]. After that, it was ground with a laboratory milling ball at 200–300 r/min for 5–6 h to reduce the size of particles so that they became less than or equal to 1 mm. On the other hand, the okra waste powder was sieved into four distinct particle sizes: 0.125 mm, 0.25 mm, 0.5 mm, and 1 mm [20].

2.3.1. Okra adsorbent activation

In this study, chemical activation of okra adsorbent was processed to increase the surface area of okra adsorbent for better adsorption, when the impregnation of the powdered okra waste was performed using phosphoric acid (H_3PO_4) as the impregnating agent. The okra powder was impregnated at a rate of 4: 1 (v/m) and the acid-treated adsorbent was then dried for 4 hours at 105°C; after that, it was cooled and washed with distilled water to remove residual organic and mineral matter, and then dried in an oven at 110°C for 24 hours; finally, samples were packed in an airtight container, and the adsorbent was ready for use.

2.3.2. Characterization of okra adsorbent

Characteristics of okra waste-activated carbon such as physical structure (e.g. particle size, specific surface area, porosity), chemical nature and functional groups (e.g. surface charge, pH at the point of zero charges), and mechanical properties were investigated. The prepared okra adsorbents were next analyzed using Fourier Transform Infrared (FTI), which gave information on the quality of the functional groups on the okra adsorbent's surface, such as C, H, N, and O [21].

2.4. Adsorption batch process

The present research conducted the adsorption batch process to investigate the adsorption efficiency of okra adsorbent for heavy metals in wastewater from the Petroleum Temane SASOL plant. Furthermore, the batch adsorption procedure was carried out by altering four parameters at a constant temperature of 60°C: The rotational speed of the agitator was increased from 500 to 1500 revolutions per minute (rpm), contact time of 30, 60, and 90 minutes were used, and the quantity of okra adsorbent used ranged from 0.25g to 1.5g, with particle sizes of 0.125, 0.250, 0.500 and 1.00 mm respectively. The effect of any of the abovementioned factors on adsorption efficiency was gradually changed to achieve the greatest removal percent of heavy metals in wastewater using okra adsorbent. At the same time, the other variables remained constant [22]. After each adsorption batch process at different variable changes, the wastewater samples were removed from the spent adsorbent with a micropipette after reaching the desired contact time. Therefore, the samples were filtered and then proceeded to the wet sample's digestion process for extraction and analysis.

2.5. Wastewater samples extraction

2.5.1. Sample digestion procedures

The acid digestion combination $\text{HNO}_3/\text{H}_2\text{O}_2$ was evaluated using the hot plate method with minor changes. Filtration was performed using cellulose-acetate filter paper and a syringe aroids filter (0.45 μm), and the results were then analyzed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) [23]. The samples were digested in triplicate for each procedure to quantify the closeness (precision) of the results obtained under the same conditions. The blank solutions, with identical reagents, subjected to the same treatment as the reference material were extracted before contact with okra adsorbent. The concentrations of heavy metals in blank solutions have been considered as initial concentrations of heavy metals in wastewater.

2.5.2. Hot plate digestion

As previously described, the acid mixture of HNO_3 and H_2O_2 was used for hot plate digestion. In this study, the sample to be digested was aqueous; wet digestion was performed for both blank and adsorbed wastewater samples. On the hot plate, the temperature was maintained at 120°C for 2 hours while the wastewater test sample was digested with 16 mL (12 mL HNO_3 and 4 mL H_2O_2) of 6:2 $\text{HNO}_3/\text{H}_2\text{O}_2$ mixtures. After the sample had cooled, 10 mL of deionized water was added and adequately mixed. Adding H_2O_2 to this approach was added to improve organic matter destruction. After digestion, the solutions were filtered using cellulose-acetate filter paper and a syringe aroidisc filter (0.45 μm), then transferred to a 100 mL volumetric flask and diluted to the mark with deionized water [23]. Figure 2 placed in the appendix shows how the mixture of HNO_3 and H_2O_2 was added to the bottle containing a wastewater sample and being digested on the hot plate.



Figure 2. The mixture of wastewater sample with $\text{HNO}_3/\text{H}_2\text{O}_2$ solution on the Hot Plate.

2.5.3. ICP-OES operating conditions

Based on the studies by Dimpe et al. (2015) and Didukh-Shadrina et al. (2019), Table 2 shows the operating conditions and wavelengths under which Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) has been calibrated to ensure result accuracy and traceability, as well as to validate data findings.

Table 2. Wavelengths and operating conditions used for ICP-OES calibration

RF power, Kw	1.3
Plasma gas flow, L min ⁻¹	15
Auxiliary Ar, L min ⁻¹	0.2
Nebulizer Ar, L min ⁻¹	0.8
Pump rate, mL min ⁻¹	1.5
Readings/replicate	3
Wavelength, nm	Cu:324.752, Fe:238.2014, Co:238.892, Ni:231.604, Al:308.215 , Zn:213.857 , Pb:220.353 ,Mn:257.610 and Cr:267.709

2.6. Adsorption isotherm

Destra (2013) described an adsorption isotherm as a graphical representation that shows the relationship between the amount of adsorbate adsorbed by a unit weight of okra adsorbents and the amount of adsorbate remaining in a test medium at equilibrium, as well as the distribution of an absorbable solute between the liquid and solid phases at various equilibrium concentrations. The following equations were used to calculate the removal efficiency (%) of okra adsorbent and the quantity of Cd²⁺, Pb²⁺, Cu⁺², and Zn²⁺ ions sorption at equilibrium (q_e, mg/g) [24].

$$RE(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C₀ is the initial heavy metal concentration and C_e is the effluent concentration in mg/L.

The experiments were carried out twice to confirm that the results were repeatable, and the mean of the two measurements was computed. The plot of equilibrium adsorption potentials indicated the equilibrium isotherm (variations of the parameters mentioned above versus concentration at equilibrium) [3].

$$q_e = \frac{C_0 - C_e}{\frac{m}{V}} \quad (2)$$

Where q_e: Adsorption capacity at equilibrium (mg of ions/g of Okra adsorbent), C₀: initial concentration of metal ions in solution (mg/L), C_e: equilibrium concentration of metal ions in solution (mg/L), m: dry weight adsorbent (g), V: volume of wastewater solution (L) [25].

2.6.1. Langmuir isotherm equation

Because of the high R² values and practically perfect fitting using the linearized regression form as shown in the equation below, the Langmuir equation assumes that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface [14].

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m} \quad (3)$$

Where C_e is the equilibrium concentration (mg/l), q_e is the amount (mg/g) adsorbed at equilibrium time, q_m and b are Langmuir constants related to maximum adsorption capacity (mg/g) and energy of adsorption about the heat of adsorption (L/mg), respectively.

2.6.2. Freundlich Adsorption Isotherm Equation

The Freundlich Isotherm has $1/n$ whose value is greater than 1 at all times. The value will always be between 0 and 1. In the Freundlich adsorption, the line plotted will be straight when the value between $\log p$ and $\log x/m$ is $1/n$. Freundlich Adsorption Isotherm Equation is represented in Equation 4 as follows:

$$\frac{x}{m} = K C^{\frac{1}{n}} \quad (4)$$

Where x is the adsorbate mass, m is the adsorbent mass, n and K are constants for an adsorbent and adsorbate at a temperature $1/n$ is essentially the value at high pressure and C is the concentration of adsorbate.

3. Results and Discussion

3.1. Fourier Transform Infrared (FTIR) analysis

Figure 3 shows the results of an FTIR analysis of the performance of activated carbon from okra waste. The primary goal of the FTIR analysis was to detect functional groups in Okra that had been activated by Phosphoric acid (H_3PO_4) as part of the characterization process.

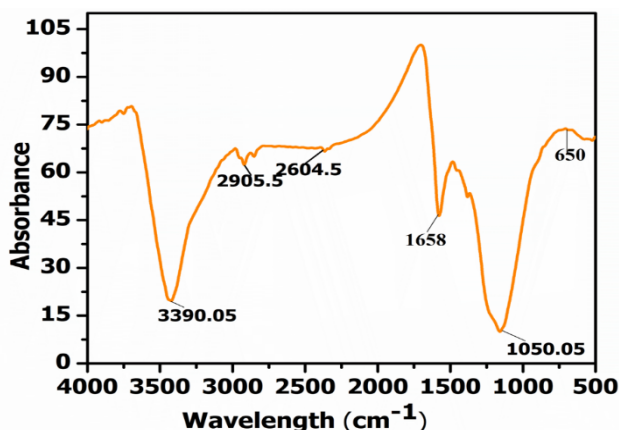


Figure 3. The infrared spectrum of okra adsorbent activated carbon

The vibration frequency alterations in the functional groups on the surface that allow the adsorption of metal ions were determined using the FTIR spectrum of okra. The spectra of adsorbents were measured in the wave number range of 500 to 4000 cm^{-1} . The FTIR analysis results shown in Figure 3 suggested the presence of functional groups such as carboxylic acid or alcoholic O-H bond stretching, which may overlap with amine (N-H) bond stretching at peaks between 3700-3200 cm^{-1} ; possible C=O bond of carbonyl or amide groups within 1800-1650 cm^{-1} ; C-O and O-H bond stretching of alcohol and ethers at 1300-1200 cm^{-1} of the finger-print region; C-O and O-H bond stretching [26]. However, the spectrum displayed the main stretching bands at (3390.05, 2905.5,

1640-1658, 1050.05 and 650) cm^{-1} which were detected to be Hydroxyl (OH), Amino (N-H), Carboxyl (C-O-C, C=O), C-O stretching and M-O groups, respectively. This study targeted removing heavy metal ions such as Cadmium, Copper, Lead and Zinc. These metal ions all have a positive charge, whereas the functional groups in okra have a negative charge due to two electrons in the oxygen and nitrogen atoms.

Adsorption by okra waste was made feasible by the lone pair of electrons on oxygen and nitrogen atoms, which supplied electrons to electron-deficient positively charged metals, allowing for the removal of positively charged metals such as Cadmium, copper, Lead, Zinc, Silver, and Barium ions [22].

3.2. Effects of adsorption parameters on heavy metals removal from natural gas production wastewater

The blank solution was prepared and analyzed under Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OAS). The initial concentration for Cd, Cu, Pb, Zn, Ag and Ba metal ions in wastewater was 125 mg/l, 1001 mg/l, 1600 mg/l, 1000 mg/l, 125 mg/l and 2375 mg/l respectively. The equilibrium concentration and the removal percentage of each metal ion onto four different okra adsorbent particle sizes 0.125 mm, 0.250 mm, 0.500 mm and 1.00 mm were both obtained by varying three adsorption parameters such as agitation speed, contact time and amount of adsorbent.

The results which showed the effect of each adsorption parameter for Cd, Cu, Pb, Zn, Ag and Ba metal ions removal onto okra adsorbent from wastewater are described below.

3.2.1 Effect of agitation speed

Figure 4 shows the effect of agitation speed on % removal of cadmium, copper, lead, zinc, Silver and Barium ions onto four different okra waste particle sizes investigated at variant agitation speeds of 500, 1000, and 1500 revolutions per minute.

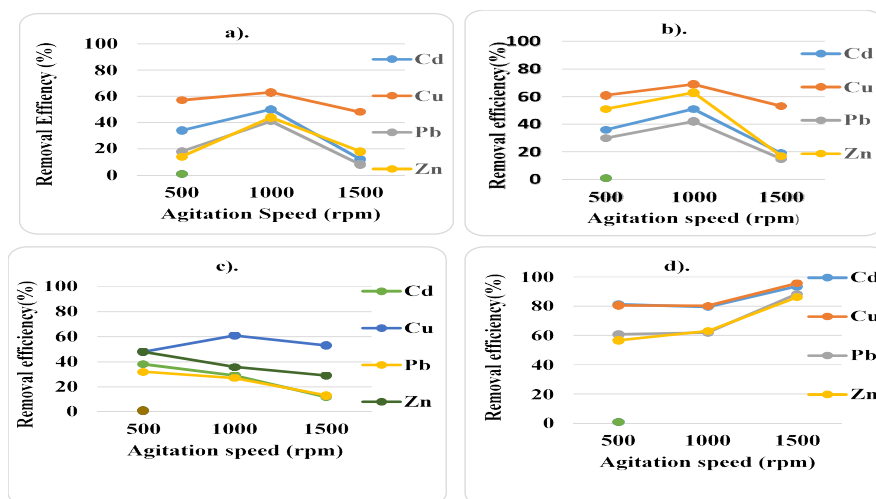


Figure 4. Effect of agitation speed for Cd, Cu, Pb and Zn metals ions removal percent onto okra adsorbent a) with 0.125 mm, b) with 0.250 mm, c) with 0.500 mm and d) with 1.00 mm.

The removal percentage of cadmium, copper, lead, and zinc metal ions rose when the shaking speed was raised to its maximum. The removal percentage of cadmium, copper, lead and zinc metal ions was 34, 57, 18 and 14%, respectively, at 500 revolutions per minute. It increased to 50, 63, 41 and 44% at 1000 revolutions per minute (rpm). The removal percent decreased to 12, 48, 8 and 18%, at 1500 revolutions per minute (rpm) when using okra adsorbent with a particle size of 0.125 mm, as shown in Figure 4a.

Figure 4b shows the effect of agitation speed on Cd, Cu, Pb and Zn metal ions using okra adsorbent with a particle size of 0.250 mm. The removal percentage was 36, 61, 30, 51, 56 and 98%, respectively at 500 revolutions per minute and increased to 51, 69, 42 and 63% respectively at 1000 revolutions per minute which decreased to 19, 53, 15 and 17% respectively at 1500 revolution per minute (rpm).

The effect of agitation speed on Cd, Cu, Pb and Zn metals ions using okra adsorbent with particle size 0.500 mm is shown in Figure 4c. The removal percentage was 38, 48, 52 and 48% respectively at 500 revolutions per minute (rpm) and decreased to 29, 61, 27 and 36 % for Cd, Cu, Pb, and Zn ions respectively at 1000 revolutions per minute (rpm) which decreased to 12, 53, 13 and 29% for Cd, Cu, Pb and Zn metals ions at 1500 revolution per minute (rpm).

Figure 4d shows the effect of agitation speed on Cd, Cu, Pb and Zn ions using okra adsorbent with a particle size of 1.00 mm. The removal percentage was 81, 81, 61 and 57% respectively at 500 revolutions per minute (rpm) and increased to 79 and 80% for Cd and Cu ions respectively and increased to 62 and 63% for Pb and Zn metals ions respectively at 1000 revolution per minute (rpm) which increased to 94, 96, 88 and 86 % for Cd, Cu, Pb and Zn metals ions at 1500 revolution per minute (rpm). The increment of the agitation speed increases the mobility of Cd, Cu, Pb, and Zn ions, which increases the diffusion coefficients. As a result of this, the mass transfer rate of Cd, Cu, Pb, and Zn ions to the surface of okra waste adsorbent becomes greater which directly increases the heavy metal ion removal percent. After that, agitation speed increased from 500 to 1000 revolutions per minute (rpm). Due to the fracture of the bonding between the Cd, Cu, Pb, and Zn ions and the surface site of the okra adsorbent, which causes desorption of the Cd, Cu, Pb, and Zn ions from the surface site, the removal percent is often reduced. Furthermore, because the faster agitation speed disperses the adsorbent particles throughout the solution, the adsorption period will be insufficient to allow the adsorbent to bind metal ions [15].

Therefore, instead of chemical adsorption, there is likely an increase in physical adsorption. However, because of its excellent removal effectiveness for Cd, Cu, Pb, and Zn metal ions removal from wastewater, agitation at 1000 revolutions per minute (rpm) with okra adsorbent with 1.00 mm particle is preferred.

A similar trend was reported by [15] who investigated the influence of agitation speed on the adsorption of cadmium and copper ions from wastewater in okra agricultural waste versus wheat bran. The results showed that when using wheat bran and okra waste, the adsorption percentage for cadmium and copper ions was 45.8 and 23.4 respectively at 50 revolutions per minute, and increased to 59.6 and 34.7 respectively at 150 revolutions per minute. The shaking speed of 150 revolutions per minute was recommended as the best for removing cadmium and copper ions from wastewater using wheat bran and okra waste.

These tendencies in results are also corroborated by earlier research [24], where they investigated the removal of Cr(III) and Cr(VI) from contaminated water using okra leaves—agricultural waste, and found that the adsorption of both chromium species (Cr(III) and Cr(VI) rose to 200 rpm (20%) before decreasing at high shaking. These findings are consistent with those discovered by [27]. His research looked at the equilibrium, kinetics, and thermodynamics of biosorption of zinc ions from industrial wastewater using walnut shell-derived composite biosorbents. The results showed that the removal efficiency of Zn (II) ions using the four prepared adsorbents increased as the agitation speed increased until it reached the optimum value, then decreased as the agitation speed increased further.

3.2.2. Effect of contact time

In an adsorption system, the contact time is critical regardless of the other experimental factors that impact adsorption kinetics. In the adsorption batch method, the removal percentage of cadmium, copper, lead, zinc, silver, and barium ions from wastewater was examined at varied contact durations ranging from 30 to 90 minutes. Figure 5 depicts the link between the removal percentage of cadmium, copper, lead, and zinc ions on four different okra particle sizes and adsorption time.

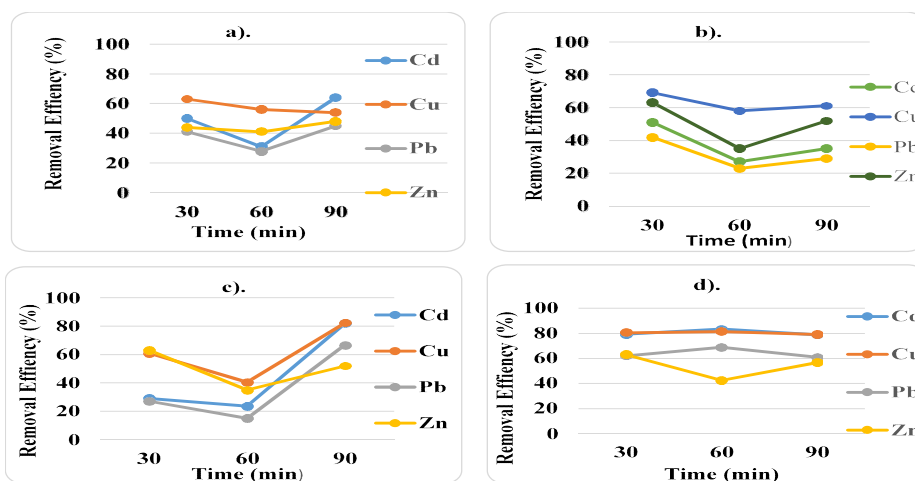


Figure 5. Effect of contact time for Cd, Cu, Pb and Zn metals ions removal percent onto okra adsorbent a) with 0.125 mm, b) with 0.250 mm, c) with 0.500 mm and d) with 1.00 mm.

Figure 5a shows the effect of contact time removing cadmium, copper, lead and zinc metal ions onto okra adsorbent with 0.125 mm particle size. The removal percentage was 50, 63, 41 and 44% respectively at 30 min and decreased to 31, 56, 28 and 41 % respectively and increased to 64, 54, 45 and 48 % respectively at 90 min.

Figure 5b shows the effect of contact time on Cd, Cu, Pb and Zn metal ions onto okra adsorbent with a particle size of 0.250 mm. The removal percentage was 51, 69, 42 and 63% respectively at 30 min and decreased to 27, 58, 23 and 35% respectively at 60 min and 90 min and increased to 35, 61, 29 and 52 % respectively at 90 min. Figure 5c shows the effect of contact time on Cd, Cu, Pb and Zn metal ions using okra adsorbent with a particle size of 0.500 mm. The removal percentage of Cd, Cu, Pb and Zn metal ions was 29, 61, 27 and 36%, respectively at 30 min. All the removal percentage decreased at 60 min along with an increment to 82, 82, 67 and 69 %, respectively for Cd, Cu, Pb and Zn metal ions at 90 min. Figure 5d shows the effect of contact time on Cd, Cu, Pb and Zn ions using okra adsorbent with 1.00 mm particle size. The removal percentage was 79, 81, 62 and 63%, respectively at 30 min and increased to 84 and 69% for Cd and Pb ions, remained constant at 81% for Cu ions along with decreased to 43% for Zn ions.

These findings may be deduced as follows: The percentage removal of metal ions increases with increasing contact time, as seen by the rate of adsorption on the surface of okra adsorbent; this tendency is because adsorption processes are rapid until they reach their optimal durations. The availability of substantial surface areas on the okra adsorbent is responsible for this phenomenon. After the equilibrium periods were reached, the adsorbent's surface pores became enclosed and subsequently, desorption occurred. The slower rate of adsorption at this stage, also known as the desorption phase, might be attributed to metal ions accumulating on the okra adsorbent's surface.

Furthermore, the removal percentage of Cd, Cu, Pb, and Zn metal ions on the okra adsorbents remained constant as the agitation time was increased from 500 pm to 1000 rpm due to the achievement of the equilibrium state, which occurs when the active centers are saturated. This happens when the ability to absorb more Cd, Cu, Pb, Zn, Ag, and Ba ions is exhausted.

Therefore, the adsorption of Cd, Cu, Pb and Zn ions on okra adsorbent with 1.00 mm particle size at 90 minutes was chosen for the later experiments to remove Cd, Cu, Pb and Zn ions from wastewater using okra waste as adsorbing the material. The findings in Figure 5 which shows the trends of contact times effect on four okra adsorbent particle sizes for Cd, Cu, Pb and Zn ions removal, are in the same line with the previous study reported by [15] who studied the removal of cadmium and copper by using okra waste and found the best time was 90 min. The trend was reported by [28] who used lignite as a low-cost material to investigate the influence of contact time on removing Cadmium and Copper ions from aqueous solutions. His findings demonstrated that minimal contact durations of 5 and 20 minutes for Cd and Cu respectively, may be employed in real-world applications to remove more than 80% of the adsorbed Cd or Cu levels.

3.2.3. Effect of adsorbent dose

The dose of okra adsorbent is critical since it influences the capacity of the adsorbent. The effectiveness of the adsorption process was shown to be influenced by the amount of adsorbent used. The okra adsorbent dosage for batch studies was tuned utilizing ranges of 0.25–1.5g for Cd, Cu, Pb, and Zn metals ions to improve its removal effectiveness due to its direct impact on adsorption performance. By shaking different volumes of okra wastes with varying particle sizes, this parameter was improved in conjunction with the other optimized parameters (Contact time=30 min, agitation speed=1000 rpm), and the results are shown in Figure 6.

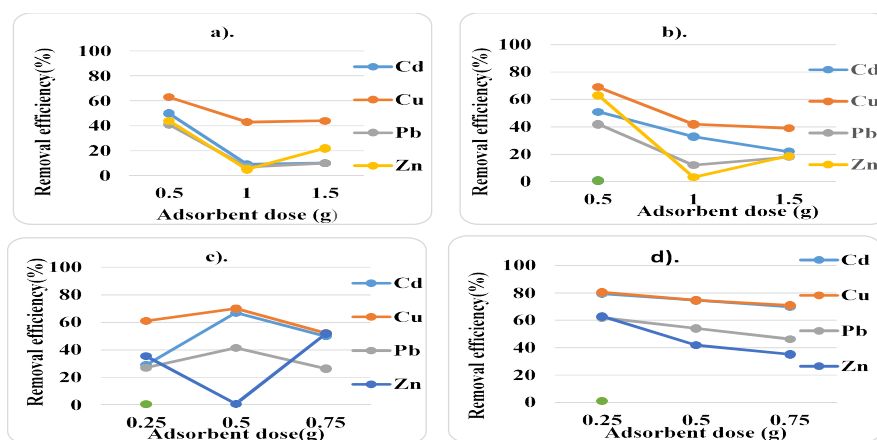


Figure 6. Effect of adsorbent dose for Cd, Cu, Pb and Zn metals ions removal percent onto okra adsorbent a) with 0.125 mm, b) with 0.250mm, c) with 0.500mm and d) with 1.00mm.

The effect of the adsorbent dose on Cd, Cu, Pb and Zn ions removal onto okra adsorbent with a particle size of 0.125 mm is shown in Figure 6a. The removal percentage attained at adsorbent dosage 0.5 g/15 mL was 50, 63, 41 and 44% for Cd, Cu, Pb, and Zn ions respectively and decreased to 9, 43, 7 and 5 % respectively at adsorbent dosage 1g /15ml, and increased slowly to 22, 18, 19% for Cd, Pb, Zn respectively, but decreased to 39 for Cu ions at adsorbent dosage 1.5 g / 15ml.

The effect of the adsorbent dose on Cd, Cu, Pb and Zn ions using okra adsorbent with particle size 0.250 mm is shown in Figure 6b. The figure shows the removal percentage was 51, 69, 42 and

63% respectively at adsorbent dose 0.5g /15ml and decreased to 33, 42, 12 and 3.3 % respectively at the adsorbent dose 1g / 15 ml and decreased to 22 and 39% for Cd and Cu respectively and increased slowly to 18 and 19 % for Pb and Zn ions respectively at adsorbent dose 1.5g / 15 ml. Figure 6c shows the effect of adsorbent dose on Cd, Cu, Pb and Zn ions using okra adsorbent with the particle size of 0.500 mm. The removal percentage was 29, 61, 27 and 36% respectively at adsorbent dose 0.25 g / 7.5 ml and increased to 50 and 52% for Cd and Zn ions respectively and decreased to 52% for Cu ion at adsorbent dose 0.5 g / 7.5 ml while it remained constant at 27% for Pb ion at adsorbent dose 0.5 g / 7.5 ml.

The effect of the adsorbent dose on Cd, Cu, Pb and Zn ions using okra adsorbent with 1.00 mm particle size is shown in Figure 6d. The removal percentage was 79, 81, 62 and 63% respectively, at an adsorbent dose of 0.25 g / 7.5 ml and decreased to 75, 75, 54 and 42 % for Cd, Cu, Pb and Zn ions respectively at an adsorbent dosage of 1g / 7.5 ml, but decreased to 70, 71, 46, 35 for Cd, Cu, Pb, and Zn ions respectively. These results may be interpreted as follows: Generally, the effect of okra adsorbent dose on removal percent for Cd, Cu, Pb, and Zn ions removal in wastewater increases with increasing the okra amount for okra adsorbent with small particle size and decreases with increasing the okra adsorbent amount with large particle size. The trend of increase in removal capacity can be associated with the availability of more adsorption sites for the metal ions [29]. This occurred due to the accumulation of a number of unsaturated binding active sites available for adsorption when the adsorbent dosage is increased. As a result, the number of Cd, Cu, Pb, and Zn ions in wastewater solution became inadequate in comparison to the binding sites available.

Furthermore, increasing the adsorbent mass beyond a certain point promotes the agglomeration of adsorbent particles, resulting in a reduction in the total surface area of the adsorbent exposed to the adsorption process and an increase in the diffusion path length [30]. Therefore, 0.25 g of okra adsorbent with 1.00 particle size was the optimal adsorbent dose to achieve the optimal percentage removal and adsorption capacity for Cd, Cu, Pb and Zn ions removal. In addition, Ba ions are highly removed on all four adsorbent particle sizes doses (0.25g-1.5g).

These results are in alignment with a previous study reported by [24] who used okra adsorbent for removal of Cr (III) and Cr (VI) from contaminated water, and their results showed that the removal percent almost increased 20% as the amount of adsorbent increased from 50 mg to 100 mg and they found that 100 g dose was better for further studies and the findings of this study are in the same line with the previous study done by [3] who studied the effect of *Eucalyptus camdulensis*—Derived Biochar doses for Adsorption of Ni^{2+} and Pb^{2+} from Synthetic Wastewater: Kinetic and Isotherm Studies. According to their findings, the best EU-biochar dosages for Ni^{2+} and Pb^{2+} removal percentages and adsorption capacity were 0.6 g and 0.15 g, respectively. A similar pattern was seen by [31] They investigated the impact of okra waste dosage on lead ion removal from aqueous solution by adsorption and discovered that the percentage of lead removed increased as the okra quantity was increased for groups of various particle sizes.

3.2.4. Effect of particle size

In the adsorption process, particle size is a crucial factor. Figure 7 depicts the equilibrium adsorption capacity of four distinct kinds of okra adsorbent particles for the removal of Cd, Cu, Pb, and Zn metal ions.

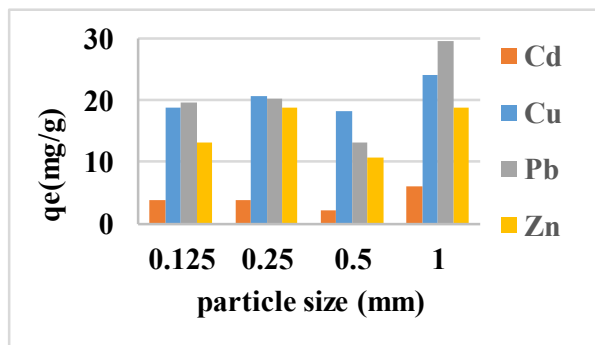


Fig.7. Effect of okra adsorbent particle size on Cd, Cu, Pb, and Zn metal ion equilibrium capacities (at constant conditions: The agitation speed is 1000rpm, and the contact time is 30 minutes).

The adsorption capacities onto okra adsorbent with 0.125 mm particle size were 3.765, 18.87, 19.665 and 13.23mg/g for Cd, Cu, Pb and Zn ions respectively. From these results, the decreasing order of Okra adsorbent with 0.125 mm for the metal ions removal was $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$.

The adsorption capacities onto okra adsorbent with 0.250 mm particle size were 3.795, 20.73, 20.235, and 18.9 mg/g for Cd, Cu, Pb and Zn ions respectively. From these results, the decreasing order of Okra adsorbent with 0.25 mm for the metal ions removal was $Cu^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+}$.

On okra adsorbent with 0.500 mm particle size, the adsorption capacities were 2.175, 18.33, 13.05, and 10.695 mg/g respectively. From these results, the decreasing order of Okra adsorbent with 0.500 mm for the metal ions removal was $Cu^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+}$. The adsorption capacities onto okra adsorbent with 1.00 mm particle size were 5.9535, 24.09, 29.73 and 18.87mg/g for Cd, Cu, Pb and Zn ions respectively. From these results, the decreasing order of Okra adsorbent with 1.00 mm for the metal ions removal was $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$.

The results of the affinity of different okra adsorbent particle sizes for the removal of Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} ions show that the okra adsorbent with 0.125 and 1.00 mm particle size had the same order for heavy metals removal, which was $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$ for both 0.125 and 1.00 mm adsorbent particle size and the results also show that Pb^{2+} ion was highly removed on okra adsorbent 0.125 mm and 1.00 mm particle with 19.665 mg/g and 29.73 mg/g of the adsorption capacity (qe) respectively whereas Cu^{2+} ion was highly removed on okra adsorbent 0.250 mm and 0.500mm particle size with 20.73 mg/g and 18.33mg/g of the adsorption capacity (qe) respectively and the Cd^{2+} ion was more least removed on all four okra adsorbent particle sizes. These results may be interpreted as follows: Figure 7 shows that the adsorption capacity for Cd^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+} ions increased as increasing okra adsorbent particle size and decreased in some cases. As a result, the greater the adsorption rate of the okra adsorbent, the smaller the particle sizes of the adsorbent. The adsorption capacity rises as the particle size decreases. Therefore, the okra adsorbent with 0.125 mm adsorbed more amount than the okra adsorbent with a larger particle size, such as 0.500 mm of particle size. This happened due to the surface as the particle size lowers, the area rises [32].

A similar trend was reported by [28] who looked at using lignite as a low-cost material for removing cadmium and copper from aqueous solutions. They discovered that the lignite with particle size less than 63 m had the highest adsorbed amount of Cd (26.1 mg/g) and Cu (18.6 mg/g), which was very small, and that when lignite particles of 1–2 mm size were used, these adsorbed Cd and Cu amounts decreased by about 25% and more than 65%, respectively. This result might be explained by the reduced microporosity and surface area found in coarser media.

3.3. Adsorption Isotherm

At the equilibrium state of an adsorption system, the adsorption isotherm was a mathematical model that characterized the distribution of adsorbate species among the liquid and solid phases. The Langmuir adsorption isotherm has been widely employed for the adsorption of a solute from a liquid solution and has been effectively used in several pollutant adsorption procedures. The Langmuir model is based on the idea that adsorption occurs at certain homogenous locations inside the adsorbent. Using equation (2), the equilibrium adsorption capacity for Cd, Cu, Pb, and Zn ions removal using several kinds of okra adsorbent particles was estimated.

3.3.1. Langmuir isotherm

The Langmuir adsorption isotherm assumes that monolayer adsorption occurs at all homogeneous surface sites, with no adsorbed molecules interacting with neighbouring adsorption sites. The linear Langmuir model may be stated as follows in linear form:

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e \quad (5)$$

where C_e is the equilibrium concentration (mg/l), q_e is the amount (mg/g) adsorbed at equilibrium time, and Q_{max} and K_L are Langmuir constants related to maximum adsorption capacity (mg/g) and energy of adsorption related to the heat of adsorption (L/mg), respectively.

Figure 8 depicts the plot of C_e/q_e versus C_e for the removal of heavy metal ions (Cd (II), Cu (II), Pb (II) and Zn (II)) by using the okra adsorbent with different particle sizes.

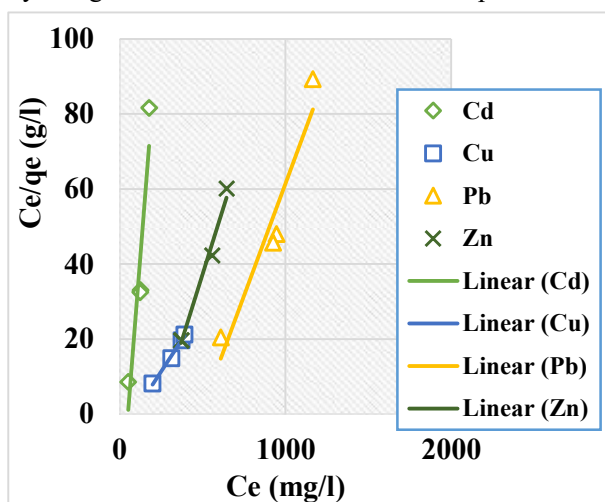


Figure 8. Langmuir isotherm for Cd (II), Cu (II), Pb (II) and Zn (II) metal ions removal at various concentrations.

From the plot, it is noticed that the sorption data are adequately fitted to the Langmuir equation with average regression coefficients ($R^2 = 0.8884-0.995$). The Langmuir parameter was computed from the slopes and intercepts of the linear plot of C_e as the x-axis and C_e /q_e as the y-axis, as displayed in Figure 8.

$$q_{max} = \frac{1}{\text{Slope}} \quad (6)$$

$$b = \frac{1}{\text{Intercept} \times q_{\max}} \quad (7)$$

The Langmuir isotherm parameters, on the other hand, were utilized to compute the affinity between the adsorbent and the adsorbate via the dimensionless separation factor, R_L , as derived by the following equation:

$$R_L = \frac{1}{(1 + bC_i)} \quad (8)$$

Where b is the Langmuir constant and C_i is the initial concentration of metal ions. The R_L values indicate whether adsorption is irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear or unfavorable ($R_L = 1$ or $R_L > 1$), or linear or unfavorable ($R_L = 1$ or $R_L > 1$)[33].

Table 3. Langmuir isotherm constants for the removal of Cd, Cu, Pb and Zn ions from wastewater by okra adsorbent.

		<i>Metals ions</i>			
<i>Isothermal modal</i>	<i>Langmuir parameters</i>	<i>Cd²⁺</i>	<i>Cu²⁺</i>	<i>Pb²⁺</i>	<i>Zn²⁺</i>
<i>Langmuir Isotherm</i>	<i>q_{max}(mg/g)</i>	1.79	14.8	8.368	7.092
	<i>K_l (L/mg)</i>	15.4	0.363474	6.924308	4.709
	<i>R_l</i>	0.00026	0.00274	9.02E-05	0.00021
	<i>R²</i>	0.8884	0.995	0.9214	0.9837

According to the literature, the equation is as follows: Linear: $R_L = 1$; Favorable: $R_L < 1$; Irreversible: $R_L = 0$. Table 3 shows the Langmuir constants found, and the Langmuir isotherm provided a superior match to the experimental data with stronger correlation coefficients (R^2) for all metal ions belonging to the range of (0.8884-0.995), wherever the maximum adsorption capacity of okra adsorbent for Cd^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+} metal ions were 1.79, 14.8, 8.368 and 7.092mg/g respectively as indicated in Table 7. The maximum adsorption capacities of the okra adsorbent were found to be between 0.363474 and 15.4 mg/g. The values for R_L in the range of 0–1 decreased with increasing initial metal ion concentration, which indicated favorable uptake of metal ions. However, the R_L value in the present study for Cd^{2+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Ag^{2+} and Ba^{2+} were found to be 0.00026, 0.00274, 9.02E-05, and 0.00021 respectively, the calculated equilibrium parameter, R_L , of the Langmuir isotherm was in the range between 0 and 1 for all the four heavy metal ions removed. Therefore, these values of R_L obtained indicated that the adsorption of the Cd^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+} metals ions onto okra adsorbent was favorable.

4. Conclusions

The okra agricultural waste adsorbent was shown to be the most efficient in removing cadmium, copper, lead and zinc metal ions from wastewater in the current study. FTIR was used to analyze the functional groups present in okra adsorbent that is responsible for the cadmium, copper, lead, zinc, silver and Barium ions removal from wastewater solution; the peaks showed the presence of functional

groups such as Hydroxyl (OH), Amino (N-H), Carboxyl (C=O, C-O-C), C-O stretching and M-O. Moreover, the batch adsorption method was performed depending on the variation of agitation speed, contact time, adsorbent dosage and adsorbent particle size, and the analysis was carried out using inductively coupled plasma – optical emission spectrometry (ICP-OES).

The optimum value of adsorption parameters for maximum removal of Cd, Cu, Pb and Zn metal ions in wastewater solution (with initial concentrations of 125 mg/l, 1001 mg/l, 1600 mg/l, 1000 mg/l in wastewater solution, respectively) was achieved using an agitation speed of 1000 rpm, a contact time of 90 minutes, and an okra adsorbent dose. However, the Langmuir isotherm model gave a better match to the experimental data with stronger correlation coefficients (R^2) for all metal ions belong between (0.8884-0.995) and the maximum adsorption capacity of okra adsorbent for Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} metal ions belong between 1.79 and 14.8 mg/g respectively. According to the linear isotherm plot, the R_L values in the present study were found to be less than one, revealing that Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} ion's adsorption to the okra adsorbent was favorable.

Based on the findings of this study, readily available okra agricultural wastes, which are a nuisance to the environment, could be used as a natural adsorbent due to their high removal efficiencies for Cd^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+} metal ions, as well as the undeniable advantages of the okra adsorbent, such as its inexpensive preparation method and easy separation when using an adsorption batch process.

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