Removal of some contaminants from River Jakara using iron oxide nano particles prepared from Citrullus lanatus Fruit Waste

Paul Ocheje Ameh
amehpaul199@gmail.com
Nigeria Police Academy

Mohammed A. Habila
King Saud University

Rajni Garg
Galgotias College of Engineering & Technology, Greater Noida (UP)

Onyima Christian
Nigeria Police Academy

Godwin O. Ihegboro
Nigeria Police Academy

Chimaobi James Ononamadu
Nigeria Police Academy

Rishav Garg
Galgotias College of Engineering & Technology, Greater Noida (UP)

Zainab Adamu
Nigeria Police Academy

Udeh Jideoliseh Joel
Nigeria Police Academy

Racheal Showunmi
Nigeria Police Academy

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Removal of some contaminants from River Jakara using iron oxide nanoparticles prepared from *Citrullus lanatus* Fruit Waste

Paul Ocheje Ameh\(^a\), Mohammed A. Habila\(^b\), Rajni Garg\(^c\) Onoyima Christian\(^a\), Godwin O. Ihegboro\(^d\), Chimaobi James Ononamadu\(^d\), Rishav Garg\(^e\), Zainab Adamu\(^a\), Udeh Jideoliseh Joel\(^d\) and Racheal Showunmi\(^a\)

\(^a\)Department of Chemistry, Nigeria Police Academy, Wudil, P. M B. 3474, Kano State Nigeria  
\(^b\)Department of Chemistry, College of Science, King Saud University, Riyadh, Saudi Arabia 
\(^c\)Department of Applied Science and Humanities, Galgotias College of Engineering & Technology, Greater Noida (UP), 201310, India 
\(^d\)Department of Biochemistry and Forensic Science, Nigeria Police Academy, Kano State Nigeria 
\(^e\)Department of Civil Engineering, Galgotias College of Engineering & Technology, Greater Noida (UP), 201310, India 

Corresponding E-mail: amehpaul99@gmail.com (ORCID ID): 0000-0002-7050-6715

**ABSTRACT**

This study investigated the applicability of iron oxide nanoparticles synthesized from *Citrullus lanatus* fruit waste (IONP) in the removal of some contaminants from water samples that were collected from River Jakara in Kano State Nigeria. The prepared nanoparticles was subjected to physico-chemical characteristic studies to determine the pH, moisture content, ash content, and porosity while the adsorbent surface characterizations was performed using Brunauer–Emmett–Teller (BET) surface area, Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and Thermogravimetric Analysis (TGA). The BET results revealed that IONP have large surface area and are nanometer sized particles. SEM analysis indicated that the adsorbent contain microsphere which might have facilitated the efficient purification of the river water while TGA study revealed that the adsorbent exhibited a three step decomposition process. Data obtained from XRD indicated that the synthesized adsorbent is of high purity and crystalline in nature with an average particle size of 17 nm.
Results obtained after treatment of the river water with the adsorbent indicated reduced values in some physicochemical parameters confirming the high adsorption ability of the prepared nanoparticles. The percentage removal of some heavy metals in the river water by IONP was found to depend on adsorbent concentration, agitation time and pH during the batch type adsorption experiments. The highest adsorption efficiency was obtained at pH = 8, temperature = 28 °C, adsorbent dosage = 200 mg/L and contact time = 100 minutes. The adsorption process of the metal ions onto the adsorbent was best described by the Langmuir isotherm model predicting monolayer adsorption and followed the pseudo second order kinetics. The regeneration stability of the adsorbent was adequate when treated with the heavy metals ions at optimum conditions. The change in the intensity of absorption as observed in the FTIR spectra of the adsorbent after treatment with the heavy metals confirms a strong interaction between the metal ions and the synthesized adsorbent. The results obtained confirm the capability of the nanoparticles synthesized from *Citrullus lanatus* waste as a new, low-cost, efficient and environmentally friendly alternative for treatment of contaminated water.

*Keywords: Citrullus lanatus, Heavy Metals, Iron oxide particles, Pollution, River Jakara*

**1.0 INTRODUCTION**

The contamination of water bodies is a serious environmental threat as that of global warming (Aziz *et al.*, 2023). Access to clean water a serious in developing countries like Nigeria as majority of the common fresh water sources available to local inhabitants are polluted (Eddy *et al* 2024; Ibrahim and Sa’id 2010). Several conventional methods that have been applied for the treatment of wastewater include reverse osmosis, precipitation, membrane separation, chemical operation, coagulation oxidation, flotation and ion exchange processes (Maftouh *et al.*, 2023).
The use of these methods for water purification have some disadvantages which include chemical usage, sludge and are practically unaffordable by the small scale industries in Nigeria. Adsorption technique has been reported to be superior among all the available methods for the removal of contaminants from water because of its low cost, simple implementation, better performance and regeneration (Abdelhamid et al 2020; Ademola et al 2019; Ahmed and Sayed 2020). Agricultural by-products such as sawdust, coconut shell, chitosan, mango leaves, egg shells have been successfully utilized as adsorbents for removing heavy metals from industrial effluents (Qasem et al 2021). Despite that these adsorbents have the ability to remove heavy metal ions from wastewater, the efficiencies and low sorption capacities limit their application deeply. The use of metal and metal oxides nano particles in heavy metal removal from aqueous solutions due to their high performance and low cost for contaminant removal is on the increase. *Citrullus lanatus* (water melon) fruit agro-wastes have been numerous studied for their heavy metal removal potential in those countries with water melon cultivation and the results revealed great functionality of those agro – waste originated adsorbents from the fruit waste (Shakoor et al 2018; Jawad et al 2018). However, literature is scanty on the development of a nano-adsorbent from *Citrullus lanatus* agro-waste to purify contaminated water from wastewater which potentially can create great opportunity for local communities as well as industrial sector. Nano materials have been proven to be very effective in the removal of contaminants in wastewater owing to large surface area to volume ratio (Mohanapriya et al 2023; Abdelatif et al 2020; Jalu et al 2021).

In this study, we carried out investigation on the adsorption characteristics of iron oxide nano particles synthesized from *Citrullus lanatus* Fruit Waste - a material without economic values, for removal of some contaminants from water samples that was collected from River Jakara.
Jakara River is the largest drainage network in metropolitan city of Kano in northern Nigeria located on longitude 8º 31' E and 8º 45' E and latitude 12º 10' N and 12º 13' N (Agbazue et al., 2015). The River which is used for irrigation, domestic use and fishing is characterized by a high level of metal contaminants as the domestic wastewater and industrial effluent from the industrial areas of the city are usually emptied into it (Agbazue et al., 2015; Jamila and Sule, 2020). The present work can provide a reference for the high value-added comprehensive utilization of *Citrullus lanatus* Fruit Waste.

2.0 MATERIALS AND METHODS

2.1 Collection of water sample from River Jakara

Water samples for physicochemical and heavy metal determinations were collected using clean airtight 1000 cm$^3$ high density polyethylene bottles around April 2023. The sample bottles used for collection have been previously soaked in 10 % HNO$_3$ overnight followed by rinsing with deionized water and the river water before use.

The water samples were filtered at point of collection, the pH taken using Jenway 3510 pH meter and there after acidified with 1.5 mL concentrated HNO$_3$ for preservation before storage in a refrigerator prior to analyses. The pretreated water samples were digested using method as described by American Public Health Association (APHA, 2022).

2.2 Physicochemical analysis of water sample

The physicochemical analysis of the water sample collected from the River before and after using the synthesized iron nanoparticle for treatment was carried out as reported elsewhere (APHA, 2022). The parameters analyzed include: temperature, pH, turbidity, Chemical Oxygen Demand (COD), Total dissolved solids (TDS), Dissolved Oxygen (DO), phosphate, chloride,
nitrate and sulphate. The heavy metal content of the water sample was evaluated using Analyst 100 Perkin Elmer Atomic Absorption Spectrophotometer.

2.3 Preparation of iron oxide nano particle from *Citrullus lanatus* Fruit Waste (IONP)

The method used in the preparation of the of iron oxide nano particles from *Citrullus lanatus* Fruit Waste was as described by Baby and Ramaprabhu (2010). Fresh water melon collected from Wudil Central market in Kano State Nigeria were washed with distilled water and there after peeled. The peel of the watermelon waste also known as watermelon rind was cut into pieces, dried and transferred into a solution containing 10 % ferric chloride hexahydrate for 24 hours. The biomass was then separated from the solution, dried in air at room temperature and thereafter subjected to pyrolysis at 450 °C for 48 hours. The pyrol treated dried mass was then charred in an oven at 105 °C and stored in desiccators for further experiment.

2.4 Characterization of the adsorbent (IONP)

Proximate analysis of IONP was implemented using the method widely reported in the literature (AOAC, 2023). Scanning Electron Microscopy analysis to determine the morphology of adsorbent were carried out using a JSM- 5600 LV scanning electron microscope produced by JEOL, TOKYO. Thermogravimetric Analysis (TGA) were performed using a SHIMADZU DTG-60H instrument under air atmosphere, with a heating rate of 20°C / min from 50 to 1000 °C to determine the thermal properties of the synthesized IONP. The specific surface area, pore volume and pore size distribution of the synthesized nanoparticle were determined by Brunauer–Emmett–Teller (BET) surface area analysis using a Automated Gas Sorption Analyzer (Model Nova Station A , Quatachrome Instrument USA) under nitrogen gas at a temperature of 77 K.
X-ray diffraction (XRD) analysis was obtained using a Panalytical X’Pert Pro X-ray diffractometer (Netherlands) equipped with a Cu-Kα monochromatic source (1.54 Å), operating at a voltage of 40 kV and a filament current of 40 mA. Agilent Cary 630 FTIR machine was used to identify the functional groups present in IONP from the characteristic frequencies on the spectra. The pH of the aqueous solution was monitored using Jenway 3510 pH meter

2.5 Determination of sorption performance by the synthesized nanoparticle

The procedure used in the determination of sorption performance by the IONP is as reported by Magudeswaran et al (2020) but with some modifications. The prepared nanoparticles were used as a filter in sand beds of height 20 cm. The thickness of nanoparticle layer over the sand bed was maintained at 4 cm. The river water collected from Jakara were passed through this filter medium and the filtrate was collected on a beaker placed over a magnet to remove the iron oxide nanoparticles if any present in the filtered water.

The contributions of the period of contact, pH and the dosage of IONP for the removal of some heavy metals from the river water were investigated by varying these factors over reasonable ranges. Residual heavy metal ion concentration in the filtrate (after adsorption) was measured Atomic Absorption Spectrometer (Model: Analyst 100 Perkin Elmer).

The amount of metal ions adsorbed in milligram per gram of the adsorbent and percentage of metal ion removed from solution was evaluated using equation 1 and 2 respectively ( Ameh 2022).

\[ \text{Amount of metal ion absorbed (mg/g)} = \frac{C_{\text{initial}} - C_{\text{final}}}{M} \times V \]  

\[ \text{Percentage metal ion removed (\%)} = \frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \times 100 \]  

\( C_{\text{initial}} \) and \( C_{\text{final}} \) are the initial and final concentrations in mg/l of metal ion in solutions, M is the mass in grams of the adsorbent and V is the volume in Litres of the effluent solution.
IONP regeneration performance was carried as reported by Chengtao et al (2022).

3.0 RESULTS AND DISCUSSION

3.1 Characterization of the iron oxide nano particles prepared from Citrullus lanatus fruit waste (IONP)
The result obtained from the proximate analysis of IONP is as presented in Table I. The pH of adsorbent is usually one of the important parameter for evaluating a good absorbent. According to Essien et al (2023), high pH indicates that the adsorbent is highly contaminated while very low pH implies that acid wash of the adsorbent was incomplete. The pH of nanoparticle in our current investigation was found to be 6.6. Most researchers recommend that for the pH of adsorbents used for treatment of wastewater and purification of drinking water should be between 6 to 8 (Jalu et al 2021).

The moisture content of the synthesized nanoparticle was found to be 7.7 %. Although the moisture content of an adsorbent has no effect on its adsorptive power, it can dilute the action of activated carbon which can imposes the use of additional weight of the carbon during treatment process leading to decrease in its adsorption efficiency. The value of moisture content reported in the current investigation is within the range reported for most good adsorbents (Essien et al, 2023).

The ash and volatile matter content was found to be 8.0 % and 40.1 % respectively. Volatile matter is due to the presence of highly porous organic compounds present in the raw material. High value of ash and volatile matter implies higher quality of the adsorbent for higher removal efficiencies (Jawad et al., 2018, Jalu et al 2021). The volatile content of the synthesized adsorbent in this study was found to be slightly higher than the minimum value recommended by other researchers for good adsorbents (Sud et al., 2008).
Bulk density is the mass of carbon that can be contained in a filter of a given solid capacity and the amount of treated liquid that can be retained by the adsorbent. The higher the density, the better the filterability of activated carbon (Odiongenyi et al., 2023). According to ASTM D 4069 (2020), the minimum value of bulk density for good adsorbents used in waste water treatment should be around 0.25 g/mL. Higher bulk density also imparts more mechanical strength. The bulk density obtained for the synthesized IONP is 0.44 g/mL. Porosity which is the main factor for increasing the adsorptive power of an adsorbent can be defined as the number of pores present in a sample. The porosity of the synthesized adsorbent was found to be 74.2 % which is higher than the values reported for sawdust, egg shell nano particle; cornelian cherry, apricot stone and almond shells (Sud et al 2008) . According to Jalu et al. (2021), the higher the porosity values of an adsorbent, the higher will be the adsorption characteristics that will be exhibited by it.

Table I: Results from Proximate Analysis of the synthesized adsorbent

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Synthesized adsorbent (IONP)</th>
<th>Standard values as per ASTM* (2020)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.6</td>
<td>6-8</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>7.7</td>
<td>5-8</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>8.0</td>
<td>5-15</td>
</tr>
<tr>
<td>Bulk density (g/mL)</td>
<td>0.44</td>
<td>0.25</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>40.1</td>
<td>37.5</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>74.2</td>
<td>40 – 85</td>
</tr>
</tbody>
</table>

ASTM = American Society for Testing and Materials

Simultaneous Thermo – Gravimetric analysis / Differential Scanning Calorimetry analysis was carried out to get some information on the bulk composition of the synthesized IONP material and the thermogram obtained is as presented in Figure I. From the results, it can be seen that IONP showed a three step decomposition process. The first decomposition step which could be attributed to water desorption or dehydration was observed between 100 to 250 °C. The second step which was observed between 250 and 400 °C indicated a rapid collapse in weight of the
adsorbent. This effect is obviously due to the disintegration of intramolecular interactions such as hydrogen bonds between molecules (Ahmed et al 2022). In the final step, it was observed there was no change in weight of the nanoparticle with any further increase in the temperature.

Figure I: Thermogram of IONP

Figure II A shows the surface morphology of the prepared adsorbent (IONP) while Figures II B, II C and II D presents the SEM images of the adsorbent after treatment with Pb (II), Ni (II) and Cd (II) ions respectively. The image obtained from the SEM of the prepared IONP (Figure II A) revealed that the adsorbent surface is porous. According to Eddy et al. (2023), the existence of the developed pores in an adsorbent microsphere usually facilitates efficient removal activity of heavy metal from wastewater. Examining the micrographs obtained from the Pb (II), Ni (II) and Cd (II) treated IONP revealed the formation of white patches on the adsorbent surface. This is an indication of the adsorption of the studied heavy metals on the surface of the prepared adsorbent.
The results from the Brunauer–Emmett–Teller (BET) analysis for surface area and pore characteristics IONP are presented in Table II. The values for specific surface area, pore volume and pore size of the synthesized nanoparticle were found to be 44.32 m$^2$g$^{-1}$, 0.019 cm$^3$g$^{-1}$, and 1.68 nm respectively indicating that the iron oxide nanoparticles synthesized are microporous (Dash et al., 2019). The porosity values obtained in this research is close to those reported in literature for good adsorbents (Hjiri 2020).

Table II: Surface Area and Pore distribution of IONP

<table>
<thead>
<tr>
<th>S/N</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>specific surface area (m$^2$g$^{-1}$)</td>
<td>44.32</td>
</tr>
</tbody>
</table>
The X-ray diffraction obtained for IONP is presented in Figure III. It can be seen from the figure that IONP gave five (5) characteristic diffraction peaks indicating that the synthesized nanoparticle is of high purity and crystalline in nature (Qayoom et al. 2020). The XRD peaks at 22.16°, 30.12°, 49.08°, 56.15°, and 64.26° with the phase plane of (111), (200), (220), (311), and (222) which are consistent with standard XRD data of γ-Fe₂O₃ signify the formation of iron oxide nanoparticle (Qayoom et al. 2020). Liu et al., (2014) have reported that the XRD peaks at 14°, 27°, and 49° correspond to the crystal face reflection of γ-Fe₂O₃. Bhuiyan et al. (2020) also identified the 26.16°, 35.12°, 35.12°, 49.63°, 56.64° peaks for α-Fe₂O₃ nanoparticle. The particle size of IONP (d) was calculated using Scherrer’s formula as shown in Equation 3

\[ d = \frac{0.94 \lambda}{\beta \cos \theta} \]  

where \( \theta \) is the Bragg’s angle, \( \lambda \) is the wavelength (1.5418 Å) and \( \beta \) is the full width at half maximum of corresponding peak.

The average particle size of IONP as evaluated using equation 3 is 17 nm which further indicates that the particles of IONP are nanometer sized.
3.2 Physicochemical Properties of water samples from River Jakara

In order to determine the physicochemical properties of the River Jakara, parameters such as Total Dissolved Solids (TDS), turbidity, Chemical Oxygen Demand (COD), Dissolved Oxygen (DO), phosphate, nitrate, sulphate and temperature were analyzed. The result obtained for the analysis of the water samples collected from river Jakara before IONP treatment indicated that the values of DO, COD and phosphate in the water are 7.6 mg/L, 14.2 mg/L and 7.3 mg/L respectively. The values reported for phosphates is higher than the permissible limit of 5.0mg/L given by National Environmental Standards and Regulations Enforcement Agency (NESREA, 2021), and World Health Organization (WHO, 2022). The high phosphate level is what usually leads to excessive growth of algae in the water body and renders the water smelly and unattractive. The dissolved oxygen value is a measure of the degree of pollution by organic matter, the destruction of organic matter and the self–purification capacity of a water body. The standard for sustaining aquatic life is stipulated at 5 mg/L (WHO, 2022).

The TDS and pH values in the water sample were determined to be 738 mg/L and 8.10 respectively. The high TDS may be attributed to deposition of more organic matter from surface runoffs of domestic waste in addition to ions into the water. It has been reported that most of the
metals usually become soluble in water at low pH (Jamila and Sule 2020). At high pH, metals become insoluble therefore it could be hazardous to the environment. The alkaline nature of the waste water under study is an indication that the water from River Jakara is hazardous to environment and water livings.

The result obtained from the heavy metal analysis indicated that the mean annual Cr, Pb, Ni, Fe, Cu, Cd and Zn concentrations in River Jakara are 0.89 mg/L, 1.51 mg/L, 0.21 mg/L, 18 mg/L, 0.25 mg/L, 0.08 mg/L and 4.85 mg/L respectively. These observed values for Ni, Cd and Pb are higher than the permissible limits given by National Environmental Standards and Regulations Enforcement Agency and World Health Organization (WHO, 2022; NESREA, 2021). The high level of some of the heavy metals in the water could result from run-off containing industrial waste. Pollution of the River water by heavy metal observed in this study is consistent with the earlier findings of Jamila and Sule (2020) where the river Jakara was reported to have been polluted by heavy metals including Copper (Cu), Chromium (Cr), lead (Pb) and Cadmium (Cd). The present of these metals in high level could pose significant risk to public health especially as the water from the River is used for irrigation, domestic application and fishing.

Temperature of the River water sample was found to be 33.5 °C. Higher temperature according to Agbazue et al (2015) induces chemical and biological reactions in wastewater. It will also affect the solubility of oxygen and produces bad odour due to anaerobic reactions.

The mean nitrate, chloride and sulphate values in Jakara River were found to be 4.39 mg/L; 62.70 mg/L and 33.20 mg/L. These are within the permissible limit set by World Health Organization (WHO, 2022).
The turbidity value of the water from river Jakara was found to be 11.8 NTU which is outside the permissible limits of 5 NTU for drinking water given by World Health Organization (WHO, 2022).

In order to increase the water quality of the river, the water sample collected from the Jakara River was passed through the synthesized IONP layers. Variation of some physicochemical parameters of the water sample collected from the River before and after using IONP for treatment is summarized in Table III. It can be seen that there is a decrease in the values obtained for some of the parameters determined after treatment with the synthesized IONP. The decrease in turbidity of the water with the nanoparticle treatment for instance means that the treatment process reduces the light scattering ability of the water. This confirms that the synthesized nanoparticle highly removed the clusters of fungi and algae implying that microorganisms were removed from water. The decrease in the DO level indicates that oxygen may have been used during the treatment process or living organisms are present in the waste water which led to the decline of the dissolved oxygen levels (Idise et al 2010). Therefore it can be deduced that the treatment of the river water with IONP lead to the improvement in the quality of the water sample.

**Table III: Concentrations of some physio-chemical parameters in water samples from river Jakara river**

<table>
<thead>
<tr>
<th>S/N</th>
<th>PARAMETER</th>
<th>VALUE BEFORE TREATMENT WITH IONP</th>
<th>VALUE AFTER TREATMENT WITH IONP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Total Dissolved Solids (mg/L)</td>
<td>736</td>
<td>505</td>
</tr>
<tr>
<td>2</td>
<td>Turbidity (NTU)</td>
<td>11.8</td>
<td>4.8</td>
</tr>
<tr>
<td>3</td>
<td>Chemical Oxygen Demand (mg/L)</td>
<td>14.2</td>
<td>8.9</td>
</tr>
</tbody>
</table>
3.3 Batch Equilibrium Studies

Since the values for Ni (II), Cd (II) and Pb (II) ions in River Jakara were higher than the permissible limits for drinking water, the performance of IONP for the removal of these metal ions were investigated in batch mode using Innova 4000 incubator shaker maintained at 200 rpm under the influence of the following operating parameters: adsorbent dose, contact time and pH.

3.3.1 Effect of adsorbent dose

The result obtained from the variation of Ni (II), Cd (II) and Pb (II) ions adsorbed by IONP is as presented in Figure IV. The amount of the studied metal ions removed by the adsorbent as seen from the plots increased with increase in adsorbent dosage up till 200 mg of the adsorbent. This observed increase in percentage removal of the metal ions with increase in adsorbent dose may be due to the increase of driving forces per unit area of the prepared iron nanoparticle activated carbon (Lee et al. 2019). In other words, it can be said that the adsorption sites remained unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose. The maximum percentage removal achieved for Ni (II), Pb (II) and Cd (II) ions were 100.00, 98.24 and 99.26 respectively with 200 mg of the adsorbent.
3.3.3 Effect of contact time

Contact time is one of the key parameters for successful deployment of the adsorbent for large scale application (Kelle et al 2023). The removal efficiency of the adsorbent in this study was affected by contact time as evident in Figure V with a rapid increase with the increase in contact time up to 100 minutes. After 100 minutes, there was no significant change with increase in time at constant adsorbent dosage. This can be explained by the fact that initially, a large number of sorption sites were available and as the sorption process continued, much of the available sites were used up which slowed the process down . The exhaustion of the remaining available sites and repulsive forces developed between solute molecules and bulk phase leads to decrease in the adsorption process (Mondal and Kar 2018). This implies that the heavy metal ions diffuse towards the surface of IONP and invade its porous matrix until it became saturated.

Figure IV: Variation of amount of heavy metal ions adsorbed by IONP with adsorbent dosage
3.3.3 Effect of pH

The amount of removal of the heavy metal ions by the prepared IONP as a function of pH is depicted in Figure VI. It can be seen that the percentage of the metal ions adsorption increases with the increase in pH from 2 to 8. However, further rise in the pH did not yield any additional adsorption. The acidic medium was more favourable for the adsorption of the metal ions. High adsorption of the metal ions at low pH indicates that, the surface of IONP seems to be acidic which increase the protonation at their surfaces due to neutralization of negative charges, resulting in easier diffusion. This provides more active surface of the adsorbents and result into more adsorption at their surfaces. The adsorption of the metals ions to the IONP surface followed the order: Pb > Cd > Ni.
3.4 Adsorption isotherm

Adsorption isotherms indicate the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent under equilibrium at constant temperature (Araujo et al 2018). The relationship between the amount of the studied metal ions adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution were studied by fitting experimental data into several known isotherms (Langmuir, Freundlich, Temkin and Dubinin – Raduskevich, etc). High linear coefficient of regression values and adsorption capacities were obtained from the Langmuir plots which suggests the suitability of the isotherm model to explain the adsorption process.

The linear form of the Langmuir adsorption isotherms are as given in equation 4 (Araujo et al 2018).

\[ \frac{C_e}{q_e} = \frac{1}{bQ_m} - \frac{C_e}{Q_m} \]
where \( q_e \) is the adsorbent metal ion quantity per gram of biomass at equilibrium (mgg\(^{-1}\)), \( Q_m \) is the maximum amount of metal ion per unit weight of biomass required to form a complete monolayer on the surface bound (mgg\(^{-1}\)), \( b \) is a constant which is related to the affinity of the binding sites (lmg\(^{-1}\)), \( C_e \) is the equilibrium concentration.

\( Q_m \) and \( b \) can be respectively calculated from the slope and intercept of the straight lines plot of \( \frac{C_e}{q_e} \) versus \( C_e \). The representations of Langmuir isotherms of Pb(II), Cd(II) and Ni(II) ions adsorption at room temperature is as given in Figure VII. The parameters evaluated from the isotherms are presented in Table IV. It can be seen that the R\(^2\) values obtained were almost unity indicating the formation of monolayer is possible for all the studied heavy metals on the surface of IONP. Langmuir model is applicable when there is a strong specific interaction between the surface and the adsorbate so that a single adsorbed layer forms. Pb (II) ions has the highest “b” value, which indicates it has high energy of adsorption and further explain why the ions among the three studied heavy metals are absorbed better by the adsorbent.

The Langmuir model can be expressed in terms of a constant known as separation factor or equilibrium parameter (\( R_L \)) given by equation 5 (Guo and Wang 2019).

\[
R_L = \frac{1}{1 + bC_o}
\]  

where \( C_o \) is the initial metal ion concentration (mgL\(^{-1}\)).

It has been reported that for favorable isotherm shapes, the separation factor must have values between 0 and 1 (Ayuba and Nyijime, 2020).

The \( R_L \) results obtained in this study (Table IV) were found to be between 0 and 1. Therefore, the adsorption of the Pb(II), Cd(II) and Ni(II) by IONP was favorable.
Figure VII: Variation of $C_e/q_e$ with $C_e$ for the adsorption of some heavy metals by IONP

Table IV: Langmuir parameters for the adsorption of some heavy metals by from River Jakara water by IONP

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Slope</th>
<th>Intercept</th>
<th>Qm (mgg$^{-1}$)</th>
<th>B (lmg$^{-1}$)</th>
<th>R$^2$</th>
<th>R$_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0.8965</td>
<td>0.23336</td>
<td>1.115449</td>
<td>3.841704</td>
<td>0.9970</td>
<td>0.307336</td>
</tr>
<tr>
<td>Pb</td>
<td>1.0330</td>
<td>0.0917</td>
<td>0.968054</td>
<td>11.26499</td>
<td>0.9973</td>
<td>0.790140</td>
</tr>
<tr>
<td>Ni</td>
<td>0.8260</td>
<td>0.3963</td>
<td>1.210654</td>
<td>2.08428</td>
<td>0.9965</td>
<td>0.437699</td>
</tr>
</tbody>
</table>

3.5 Adsorption Kinetic study

Adsorption kinetic study is most important in determining the efficiency of adsorption. It can be used to predict the rate at which contaminants is removed from aqueous solution in order to design adsorption treatment plant (Ayuba and Nyijime, 2020). Kinetic models were used to test the experimental data and determine the mechanism of adsorption and its potential rate controlling step. Four different models viz: pseudo first order, pseudo second order, elovich model and intraparticle diffusion model were applied to the experimental data for this this
purpos. The validity of the order of adsorption process was based on the two criteria: regression coefficient and calculated $q_e$ values.

The pseudo first and second order equation can be expressed by equation 6 and 7 respectively (L´opez-Luna et al 2019).

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right) t$$  \hspace{1cm} 6

$$\frac{t}{q_e} = \left(\frac{1}{k_2q_e^2}\right) + \left(\frac{1}{q_e}\right) t$$  \hspace{1cm} 7

where $q_e$ and $q_t$ are respectively the amount of heavy metal ions in mg/g adsorbed at equilibrium and at time, t ; $k_1$ is the first order rate constant (min$^{-1}$) and $k_2$ is the second order rate constant (gm$^{-1}$min$^{-1}$). From equation 6, a plot of $\log(q_e - q_t)$ versus t is expected to be linear if the model is obeyed with slope and intercept equal to $k_1/2.303$ and $\log (q_e)$ respectively. The implication of equation 7 is that a plot of $\frac{t}{q_e}$ versus t should be a straight line with slope and intercept equal to $\frac{1}{q_e}$ and $\frac{1}{k_2q_e^2}$ respectively.

The linearized plots of the pseudo first order and pseudo second order kinetic models obtained from the experimental data are given in Figure VIII and IX respectively. The calculated constants from their intercepts and slopes, and their correlations ($R^2$) are summarized in Table V. From the results presented, it can be seen that the pseudo second order kinetic model provides the best correlation for all the three metal ions studied.
Figure VIII: Pseudo first order rate plots for the adsorption of some heavy metal ions onto IONP

Figure IX: Pseudo second order rate plots for the adsorption of some heavy metal ions onto IONP

Table V: Pseudo first and second order rate constants for the adsorption of some heavy metal ions by IONP

<table>
<thead>
<tr>
<th>Cation</th>
<th>qₑ (mg/g)</th>
<th>k₁ (min⁻¹)</th>
<th>R²</th>
<th>qₑ (mg/g)</th>
<th>K₂ (g·mg⁻¹·min⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>0.10752</td>
<td>0.0065</td>
<td>0.439</td>
<td>4.982561</td>
<td>0.052451</td>
<td>0.9938</td>
</tr>
</tbody>
</table>
Since the pseudo first order and pseudo-second order models could not identify the diffusion mechanism through the pores present in the surface of adsorbent, the kinetic results were further analyzed using the Elovich model. The linearized form of Elovich adsorption model is given by equation 8 (Eddy et al 2022).

\[ q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t) \]  

where \( \alpha \) is the initial adsorption rate (mg/g/min), and \( \beta \) is related to the extent of surface coverage and activation energy (g/mg).

The implication of equation 8 is that a plot of \( q_t \) versus \( \ln(t) \) should be linear with slope and intercept equal to \( \frac{1}{\beta} \) and \( \frac{1}{\beta} \ln(\alpha \beta) \) respectively. The Elovich coefficients as determined from the plots of \( q_t \) vs \( \ln(t) \) (Figure X) is as presented in Table VI. From the correlation coefficient value obtained, it is inferred that the Elovich model may not be applicable for the adsorption of selected heavy metals using IONP. This suggests that the adsorption of all three heavy metals onto the studied adsorbent is by physisorption. According to L´opez – Luna et al (2019), the Elovich equation is mainly suitable for the chemisorption kinetics.

<table>
<thead>
<tr>
<th></th>
<th>Cd(II)</th>
<th>0.10752</th>
<th>0.0065</th>
<th>0.439</th>
<th>2.715178</th>
<th>0.028352</th>
<th>0.9954</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(II)</td>
<td>0.08465</td>
<td>0.0073</td>
<td>0.8981</td>
<td>3.435246</td>
<td>0.009064</td>
<td>0.9995</td>
<td></td>
</tr>
</tbody>
</table>
The intraparticle diffusion model (which linearized form is given by equation 9) was applied to the experimental data in order to predict the rate controlling step of the adsorption process (Benkaddour et al. 2018).

\[ q_t = k_{in} \sqrt{t} + \beta \]  

where, \( k_{in} \) (mg/g min\(^{1/2}\)) is the of intraparticle diffusion rate constant and \( \beta \) (mg/g) is related to the thickness of the boundary layer, calculated from the slope and intercept of \( q_t \) vs \( \sqrt{t} \) plots respectively.

According to Revellame et al., (2020), if the intraparticle diffusion is involved in the adsorption processes, then the plot of the square root of time (\( \sqrt{t} \)) versus the uptake (\( q_t \)) would result in a linear relationship and the intraparticle diffusion would be the controlling step if this line passed through the origin. When the plots do not pass through the origin; this is indicative of some degree of boundary layer control and this further show that the intraparticle diffusion is not the only rate controlling step, but also other processes may control the rate of adsorption (Kostoglou and Karapantsios, 2022). In our study, a good linearity was obtained for plot of \( q_t \) vs \( \sqrt{t} \) (Figure X).

**Figure X: Elovich plots for the adsorption of some heavy metal ions onto IONP**

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where, \( k_{in} \) (mg/g min\(^{1/2}\)) is the of intraparticle diffusion rate constant and \( \beta \) (mg/g) is related to the thickness of the boundary layer, calculated from the slope and intercept of \( q_t \) vs \( \sqrt{t} \) plots respectively.

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XI) at varying concentrations of the studied metal ions suggesting that intraparticle diffusion mechanism is important at the initial stage of the adsorption. Kinetic parameters derived from the plot are as presented in Table VI. The values of intraparticle diffusion rate constant ($k_{in}$) obtained were discovered to be higher than those reported for some good adsorbent in literature (Benkaddour et al. 2018; Eddy et al 2022). Larger or higher $k_{in}$ values usually illustrate better adsorption which is related to improved bonding between adsorbate and adsorbent particles. Application of intraparticle diffusion model to the experimental data in our study gave a good fit plot with correlation coefficient ($R^2$) values almost unity and “$\beta$” values is less than unity which further supports an enhanced rate of adsorption (Edet and Ifelebuegu 2020).

![Figure XI: Plot of $q_t$ vs $\sqrt{t}$ for the adsorption of some heavy metal ions onto IONP](image)

### Table VI: Elovich and intraparticle diffusion rate coefficients for the adsorption of some heavy metals onto IONP

<table>
<thead>
<tr>
<th>Cation</th>
<th>$\beta$ (g/mg)</th>
<th>$\alpha$ (mg/g/min)</th>
<th>$R^2$</th>
<th>$k_{in}$ (mg/g min$^{1/2}$)</th>
<th>$\beta$ (mg/g)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>0.556886</td>
<td>-1.68371</td>
<td>0.7414</td>
<td>0.4519</td>
<td>0.7864</td>
<td>0.9829</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>2.852253</td>
<td>0.137735</td>
<td>0.9414</td>
<td>0.2645</td>
<td>0.7522</td>
<td>0.9654</td>
</tr>
</tbody>
</table>
3.5. FT-IR analysis

Numerous chemical functional groups such as carboxyl, hydroxyl, amide, ether, etc. have been identified as potential adsorption sites to be responsible for binding metallic ions to an adsorbent. Their potential for metal uptake depends on factors such as the abundance of sites, their accessibility, chemical state and affinity between adsorption site and metal (Jawad et al. 2018). The FTIR spectra for virgin and heavy metals (Cd$^{2+}$, Pb$^{2+}$ and Ni$^{2+}$) treated IONP are given in Figure XII A – D. The Peaks and functional group assignment of FTIR adsorption by the synthesized iron oxide nanoparticle and heavy metal ions treated IONP are summarized in Table VII. Examination of the FTIR spectrum of virgin IONP (Figure XII A) revealed that there a broad band at 3356 cm$^{-1}$ which can be ascribed to the stretching vibrations of surface OH groups and molecular water (Jawad et al. 2018). The absorption frequency observed at 1623 cm$^{-1}$ was assigned due to the carbonyl group (C=O) of unionized carboxylate stretching of carboxylic acid or ester while the band at 1023.15 is attributed to C – O stretch while the peak at 1689 cm$^{-1}$ was attributed due to the C=O stretching of carboxylic acid with intermolecular hydrogen bonding form. Peaks observed 779 cm$^{-1}$ were ascribable to Fe – O stretch [57]. Other peaks observed as highlighted in Table VII were attributed to the =CH out of plane, C-H wag, C-H in plane bending (CH$_3$) and C-H aliphatic stretch. The shift in absorption frequency as observed in the FTIR spectra of IONP after treatment with the heavy metals (Figure XII B, C and D) may be taken as evidence of some sort of interaction between the metal ions and the adsorbent surface. There are also the disappearance of some functional groups like “C=O stretch”, “O-H stretch” and “C-O” stretch in the heavy metal treated IONP spectra indicating the possibility that the
adsorption process could be taken place via an ion exchange process and an evidence that some
of the functional groups had been used in bond formation with the metal ions.
Figure XII: FTIR Spectra of (A) native IONP (B) Ni (II) treated IONP (C) Pb (II) treated IONP (D) Cd (II) treated IONP

Table VII: Peaks and functional group assignment of IR adsorption by the synthesized iron oxide nanoparticle and heavy metal ions treated IONP

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Functional group assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>IONP</td>
<td>Ni(II) treated</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>IONP</td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>779.013</td>
<td>711.9</td>
</tr>
<tr>
<td>872.19</td>
<td>862.9</td>
</tr>
<tr>
<td>1023.15</td>
<td></td>
</tr>
<tr>
<td>1313.88</td>
<td>1336.3</td>
</tr>
<tr>
<td>1420.12</td>
<td>1418.3</td>
</tr>
<tr>
<td>1623.25</td>
<td></td>
</tr>
<tr>
<td>2851.41</td>
<td></td>
</tr>
<tr>
<td>2920.37</td>
<td></td>
</tr>
<tr>
<td>3356.47</td>
<td></td>
</tr>
</tbody>
</table>

### 3.6. Reusability studies

The industrial use of adsorbent for large scale water treatment depends on the regeneration of surface sites on the adsorbent. The effectiveness of an adsorbent can be proved towards operational cost and ecofriendly nature through adsorption and desorption experiments. Desorption studies was carried out to explore the possibility of recycling the synthesized adsorbent and recovery of Ni(II) Pb (II) and Cd (II) ions from it. It was discovered that higher acidity favours for the desorption process. An appreciable desorption of the studied metal ions from the sorbents was achieved as seen in Figure XIII. It is worthy to note that the absorption removal rate of IONP remained almost unchanged in the first three cycles. The adsorption – desorption after the third cycle stands at 91.27, 97.11 and 93.19 for Cd (II) Pb (II) and Ni (II) respectively reflecting the high stability and economic viability of the adsorbent. A gradual decrease in the adsorption - desorption efficiency with increase in cycle number after the third
one was observed. After seven cycles, the minimum removal efficiency was 73.56 % for Cd (II) ions. This shows that IONP has good regeneration performance and can be useful for application in a continuous industrial scale operation

![Regeneration properties of IONP](image)

**Figure XIII: Regeneration properties of IONP**

### 4.0 CONCLUSION

An iron oxide nanoparticles based activated carbon was prepared from *Citrullus lanatus* Fruit Waste (IONP), characterized and applied for the removal of some contaminants from water samples that were collected from River Jakara in Kano State Nigeria. Results obtained indicated that the synthesized nanomaterial can be used to convert the contaminated river water sample into a good quality through the process of adsorption. The adsorption process followed pseudo-second order kinetics with physisorption as the adsorption route. The stability of the adsorbent was also found to be stable even after seven consecutive cycles in the waste water treatment. IONP can be regenerated and effectively used for the adsorption of heavy metals with no serious performance decline.
Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Availability of data and materials:
The datasets used or analyzed during the current study are available from Dr Ameh Paul Ocheje upon reasonable request.

Competing interests
The authors declare that they have no competing of interests.

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Author Contributions:
Paul Ocheje Ameh did the conception & designed of the work and was a major contributor in writing the manuscript. Onoyima Christian, Godwin O. Ihegboro, Chimaobi James Ononamadu, Zainab Adamu, Udeh Jideoliseh Joel, Paul Ocheje Ameh and Racheal Showunmi performed the experiment and interpreted the data; Rishav Garg wrote some parts of manuscript while Mohammed A. Habila; Rajni Garg substantively revised the manuscript. All authors read and approved the final manuscript.

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REFERENCES


Kelle HI, Ogoko EC, Akintola O, Eddy NO (2023) Quantum and experimental studies on the adsorption efficiency of oyster shell–based CaO nanoparticles (CaONPO) towards the removal of methylene blue dye (MBD) from aqueous solution, Biomass Convers. Biorefin https://doi.org/10.1007/s13399-023-04947-


L’opez-Luna J, Ram’irez-Montes LE, Martinez-Vargas S, Martínez AI, Mijangos-Ricardez OF, González-Chávez MA, Carrillo-González R, Solís-Domínguez FA, Cuevas-Díaz M,


