

Adsorption of Iron (II) from Textile Industry Effluent using *Luffa Cylindrica*

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Abstract

This research investigated the efficiency of *luffa cylindrica* activated carbon as adsorbent material in the removal of iron (II) from the textile industry effluent in a batch adsorption experiment. The adsorption process was studied as a function of contact time, pH of the solution and adsorbent dosage. At room temperature, the batch adsorption experiment showed maximum adsorption of iron (II) at a pH of 6, a contact time of 60 minutes and an adsorbent dosage of 1g/L. The effluent was characterized using the standard method (atomic absorption spectrometry) while the adsorbent was prepared, carbonated and characterized using SEM and FTIR. The SEM findings revealed a highly porous morphology. The FTIR revealed the presence of various functional groups (OH, CH, C=C and C-C). The findings of the batch adsorption experiment were fitted using Langmuir and Freundlich isotherm models and Langmuir model gave a better fit. The kinetic data of iron (II) was evaluated using pseudo-first-order and pseudo-second-order kinetic models. The batch adsorption experimental data conforms more to the pseudo-first-order kinetic model.

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Receive 03 July 2022,

Revised 04 April 2022,

Accepted 11 April 2022.

Keywords: Adsorption, *luffa cylindrica*, Iron (II), pollution, effluent.

1. Introduction

With the recent global population explosion, there has been a corresponding increase in the consumption of various forms of products, both natural and synthetic. This further leads to an increase in industrial activities, which in turn gives rise to the problem of environmental pollution of various kinds arising from waste generated by industries. Heavy metals have extensively been used in many industrial processes due to their significance. In some cases, they are found to be inherent in the raw materials used by process industries. Heavy metal pollution among the various forms of pollution caused by industrial processes is considered a significant threat to both environmental and human safety. Heavy metals and other contaminants discharged into the environment end up leaching into the groundwater and open water bodies. The metal ion in solution form is considered toxic and non-degradable. For this reason, the ingestion of amounts above the acceptable limits will lead to various health issues. Pb^{2+} , Cu^{2+} , Fe^{3+} , and Cr^{3+} are common heavy metals with the likelihood of accumulating in systems of organisms causing several ailments and disorders. [1–4]. Several techniques have been used in the removal of heavy metals from industrial effluent. Common among the methods include precipitation, membrane filtration, ion exchange, sorptive floatation and adsorption. Membrane filtration is the most effective method is having a major disadvantage of maintenance and operational cost with known susceptibility to material failure and defect development[5]. Adsorption process is commonly employed in industrial effluent treatment for the removal of heavy metal ions. Adsorption involves the use of adsorbent material, which combines with pollutants through physical and chemical forces of attraction. Adsorption is efficient both in terms of the success of the separation of heavy metal ions and the economics of implementing the technology. Several adsorbent materials such as plant fibers, minerals and macromolecules have been used [6]. In recent times, bio-adsorbents and activated carbon obtained from natural sources rich in cellulose, lignin, tannin and pectin serving as adsorption sites for heavy metal ions have been utilized widely in wastewater treatment. Activated carbons from abundant agricultural by-products permit the transformation of unwanted waste to adsorbent materials of high value[7]. Researchers have conducted several studies exploring the effectiveness of various locally sourced adsorbent materials in heavy metal ion removal from waste at a very low cost. A wide variety of readily available materials such as rice husk, bark, wheat straw, bran, tree fern, apple, dolomitic sorbents and many more have been investigated with varying degrees of successes. *Luffa cylindrica* is a lignocellulose plant material composed of 60% cellulose, 30% hemicellulose and 10% lignin by weight, and belongs to the cucurbitaceous family. It is found in abundance as agricultural remains in many countries across Asia (India, Korea, China, and Japan) and also in Africa. *Luffa Cylindrica* has a fibro-vascular stem, which is very useful in wastewater treatment, its biodegradability and renewability make it an adsorbent material of choice [2,4,7]. A study was conducted on the physical properties of *luffa cylindrica* adsorbent. Findings revealed the specific surface area (BET (m^2/g), total surface area (m^2/g), pore diameter range and bulk density (g/cm^3) to be 0.28, 1.1895, 1051.309204 to 0.003577 and 0.34 respectively. This signified that the surface area, with pore diameter and bulk density values in concordance with those found in typical mesoporous materials[8]. In this paper, adsorption of iron (II) ion from textile effluent using activated carbon was studied. Characterization of the *luffa cylindrica* and the effluent, kinetics of adsorption, effects of parameters such as adsorbent dose, pH, and contact time were carried out to determine the uptake efficiency of iron(II) removal using *Luffa Cylindrica*.

2 Materials and Method

2.1 Effluent Collection

The raw effluent was obtained from Rosie's textile factory located at Osisioma, Aba, Abia State. It was collected using a sterile 20 litres container from the point of discharge into the environment, then stored under room temperature without further purification or treatment.

2.2 Adsorbent Collection

Luffa Cylindrica was obtained from Michael Okpara University of Agriculture, Umuahia, Abia State. The seeds were removed from the sponge, and the sponge was cleaned and sun-dried for 24 hours. The dried *luffa cylindrica* was then stored in an airtight container.

2.3 Adsorbent Preparation

The dried materials were crushed and grounded into small particles; it was washed with distilled water again to remove traces of absorbed salts. It was treated with NaOH (60%) and carbonized in a muffle furnace for 4 hours at a temperature of 700°C, the furnace was cooled to room temperature and the obtained product was washed with distilled water until the pH of the filtrate is neutral. It was then dried at 100°C and sieved using a particle size of 1.5mm to obtain a fine powered of the activated carbon.

2.4 Textile Effluent Characterization

The effluent was analysed for the presence of heavy metals by digesting 100ml using 10ml of H₂SO₄ in a 250 ml conical flask placed in a fume cupboard. The concentrations of the heavy metals in the wastewater were determined using Atomic Absorption Spectrometer (AA-7000, Shimadzu, Japan)

2.5 Batch Adsorption studies

The initial pH of the textile effluent sample was taken using a pH meter (pH-2601) and a 100ml of the effluent was transferred to a 250cm³ Erlenmeyer flasks. 0.2g of luffa activated carbon (LAC) was weighed using an electronic balance (MODEL: YP502N) and added to the effluent. The solution was agitated for 10mins using a speed adjusting multipurpose vibrator (HY-2) at 100rpm after which 10ml of the solution was further centrifuged for 5mins before taking a spectrophotometer reading. Effects of adsorption parameters like adsorbent dosage, contact time, pH, and initial concentration were studied. The effect of pH on adsorption was evaluated by varying pH from 2 to 10 using 0.1M HCl and 0.1M NaOH for adjustments. The contact time was varied between 10 to 60 minutes to study the effect of time on adsorption and adsorbent dosage was varied from 0.2 g/L to 1 g/L to know the effect of dosage. For each parameter study, the solid phase was separated using filter paper and the residual metal concentration present in the supernatant was determined by Atomic Absorption Spectrophotometer (MODEL: AA-700).

2.5.1 Determination of Adsorption Capacity

The amount of metal ion adsorbed onto activated carbon at any time, q_t was calculated from:

$$q_t = \frac{(C_o - C_t)V}{W} \quad (1)$$

At equilibrium, $q_t = q_e$ and $C_t = C_e$; therefore, the amount of adsorbed metal ion, q_e , was calculated from:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

The percentage removal of ion from the aqueous solution was estimated by using

$$\%R = \frac{(C_o - C_e)100}{C_o} \quad (3)$$

Where C_o , C_t and C_e are the initial concentration, concentration at any time and equilibrium concentrations of metal ion solution (mg/L), respectively, V is the volume of the solution (L), and W is the mass of activated carbon (g).

2.6 Adsorbent Characterization

2.6.1 FTIR Analysis.

The Fourier transform infrared (FTIR) analysis of the sample was carried out to find the functional groups present on the surface of the adsorbent using the FTIR spectroscope (PerkinElmer Spectrum one v3.02 FT-IR Spectrometer, India).

2.6.2 Scanning Electron Microscope (SEM) Analysis

Scanning electron microscope (SEM) analysis of the sample was carried out to determine the morphological structure of the activated carbon before and after adsorption using (HITACHI S-5500, Japan)

3 Results and Discussion

3.1 Characterization of textile industry effluent

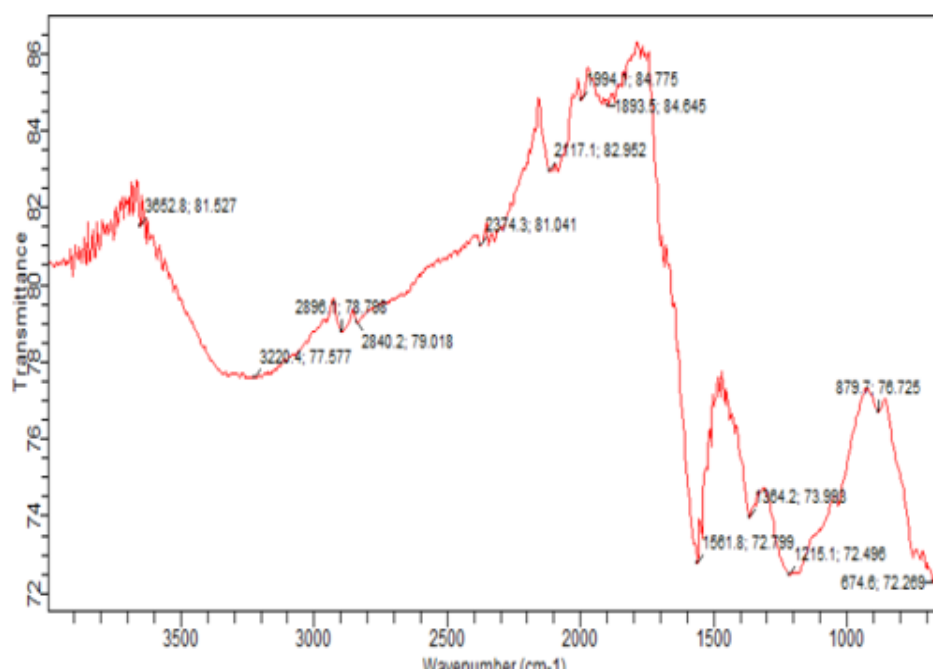
Table 1: The Physico-chemical characteristics of the textile industry wastewater.

Characteristics	Units
Color	Yellowish green
pH	6.47mg/L
Ni	0.015mg/L
Ec	400.00μs
TDS	5680.90mg/L
BOD	543.0mg/L
COD	850.00mg/L
TDC	588.09mg/L
NO3-N	1.400mg/L
Cl-1	60.27mg/L
P	12.50mg/L
Mn	38.90mg/L
Pb	0.042mg/L
Fe	38.20mg/L
Cu	0.016mg/L
Cr	0.035mg/L
Zn	1.62mg/L

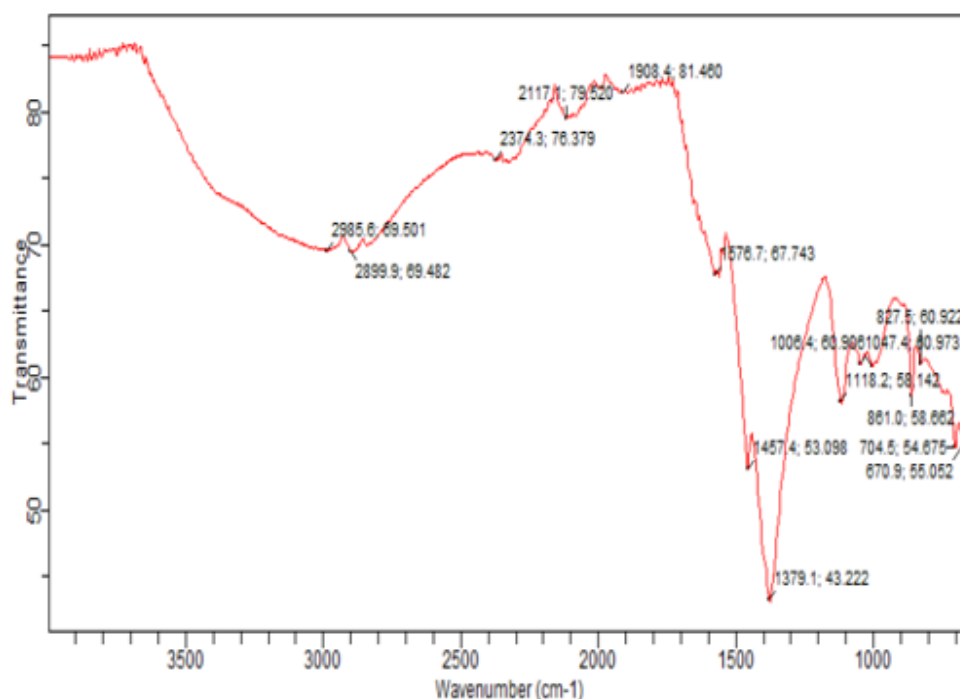
3.2 Adsorbent Characterization

3.2.1 FTIR Analysis

The FTIR spectrum of the carbonized *luffa cylindrica* before and after the adsorption is shown in Figures 1(a and b). Before the adsorption (Figure 1a), there is a clear indication of an intense peak at 3652.8 cm^{-1} attributed to the stretching of the O-H group due to inter-molecular and intra-molecular hydrogen bonding of polymeric compounds such as alcohol and phenols. The peak observed at 2896.1 cm^{-1} was associated with the stretching vibrations of CH bond of methylene groups. The peaks at 1994.1 cm^{-1} corresponded to the C=C stretching which might be attributed to the presence of aromatic or olefinic bands. The intense peak at 879.7 cm^{-1} corresponds to the C-O stretching of alcohol or carboxylic acid. After the adsorption of metal ions (Figure 1b), the FTIR spectra had shifted slightly after binding with metals. This was due to the participation of these functional groups in the binding of metal ions.



(a)

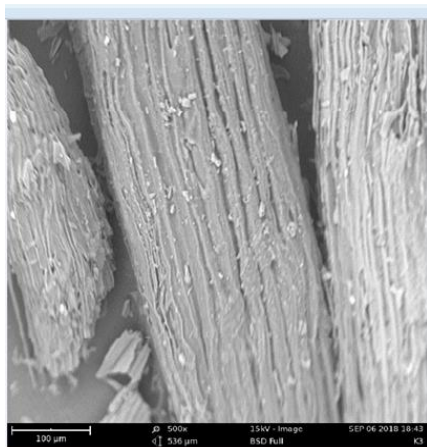


(b)

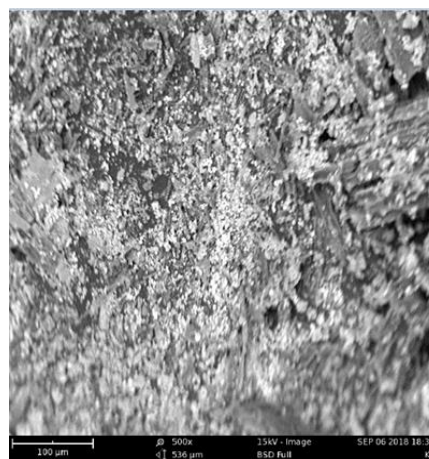
Figure 1: FTIR Spectrum for activated luffa cylindrica (a) before adsorption and (b) after adsorption

3.2.2 Morphological and Textural Examination of the Adsorbent

The SEM micrograph of *luffa cylindrica* activated carbon before adsorption is shown in Figure 2(a). It can be seen that surface of activated *luffa cylindrica* is porous. Figure 2(b) shows the SEM morphology of the activated form of *luffa cylindrica* after Fe^{2+} loading. From the figure, the surface is coarse, this indicates that a layer is formed due to Fe^{2+} adsorption on the surface and some Fe^{2+} have occupied inside the pores of the activated form of *luffa cylindrica*.



(a)



(b)

Figure 2: SEM image of the activated form of luffa cylindrica before adsorption (a) and after adsorption (b) at a magnification of 500.

3.3 Effects of contact time

Contact time defines the rate at which adsorption proceeds and how efficient a given wastewater treatment process is. Therefore, it is key to determine, under various operational conditions the dependence of the adsorption process on time[9]. The effect of contact time on the removal of iron (II) was studied using 0.2g adsorbent under room temperature. Figure (3) below shows a continued increase in the adsorption with time from 10 to 40minutes. This can be attributed to availability of the uptake pore. It is also be observed that the rate of adsorption is increased slowly between 40 to 60minutes, which can be attributed to adsorbate saturation of the adsorbent. Hence, optimal removal efficiency of iron (II) was obtained at 60minutes.

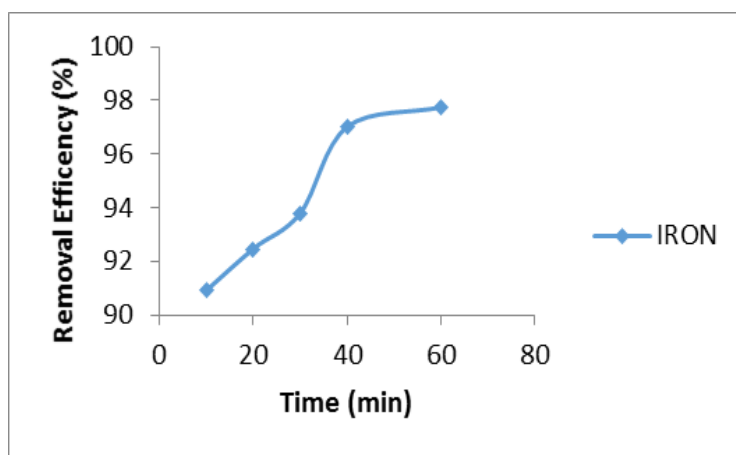


Figure 3: Effect of contact time on adsorption of Fe^{2+} using luffa cylindrica.

3.4 Effect of pH

Heavy metal adsorption from industrial effluent has been found to depend heavily on the pH of the solution containing the ions. This can be attributed to the fact that hydrogen ions are strong competing ions and partly to the fact that pH influences the chemical convergence of the metal ions and the ionization mechanism between the functional groups onto the surface of the adsorbent[10]. The effect of pH on the uptake of metal iron from the effluent was studied by varying the pH from 2 to 10 using 0.1M HCl and 0.1M NaOH for adjustment over a period of 10mins. Figure (4) below shows the variation of the adsorption rate of the metal ion with pH. The plot shows a gradual increase in adsorption rate with increasing pH from 2 to 6. This is as a result of reduced hydrogen ion competition with the metal ion for the adsorption sites and also a reduction of repulsion charge from the surface of the adsorbent towards the metal ion. It can be concluded from the plot that the optimum pH for metal ion adsorption is at a pH of 6.

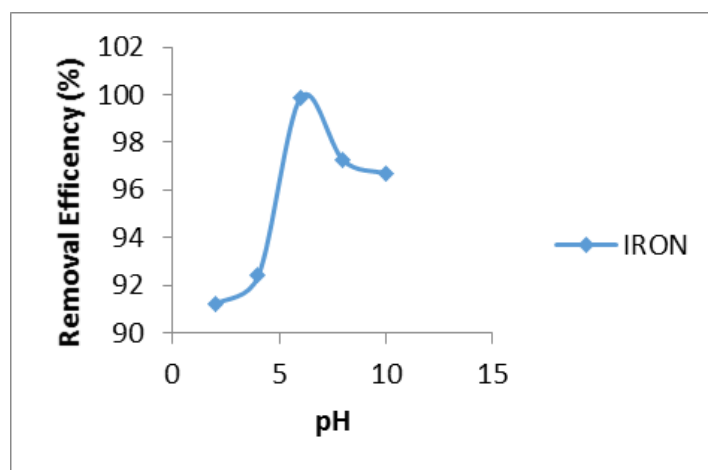


Figure 4: Effects of pH on adsorption of Fe^{2+} using Luffa Cylindrica.

3.5 Effects of adsorbent dosage

The adsorbent (luffa cylindrical) dosage was varied to determine the optimum dose at which maximum adsorption is achieved. The effect of the adsorbent dose was studied over 10mins and the adsorbent of particle size of 300 microns at doses of 0.2, 0.4, 0.6, 0.8, 1.0g was used respectively. Figure (4) shows a rapid increase in the adsorption efficiency of iron(II) ion as the adsorbent dosage increase from 0.2 to 0.4g.

A further increase in adsorbent dose indicated no significant increase in the uptake rate. This can be attributed to the fact that the increase in adsorbent dosage increases the adsorptive removal of iron (II), there is more site for adsorption leading to unsaturation adsorption sites. Besides, a reduction in adsorption density can be attributed to aggregation caused by particle interaction as a result of increased dosing of adsorbent[11,12].

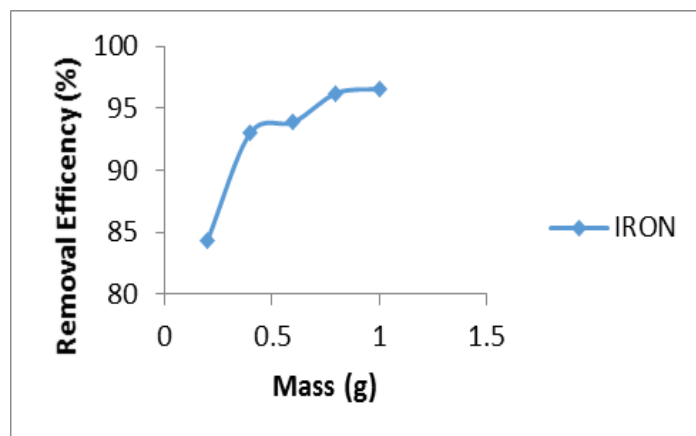


Figure 5: Effect of adsorbent dosage on the adsorption of Fe^{2+} using luffa Cylindrica

3.6 Adsorption isotherm

The mode of interaction between adsorbent molecules and metal ions and the extent of accumulation is studied using the isothermal models. Equilibrium data often termed adsorption isotherm forms the basis for the design of adsorption systems. For this study, the equilibrium data were modeled with the Langmuir and Freundlich models. The Langmuir model works based on the assumption that the monolayer adsorption takes place at the finite number of uniform sites on the adsorbent(5). The linearized form of the Langmuir equation when plotted provide a good idea on the interaction between the adsorbate and the adsorbent can be expressed as:

$$\frac{C_s}{q_s} = \frac{1}{q_m K_L} + \frac{C_s}{q_m} \quad (4)$$

Where q_m is the maximum amount of metal ion per unit mass, K_L is the Langmuir constants and C_e is the equilibrium concentration at time t ($C_e = C_t$), and q_e is the equilibrium adsorptive capacity.

The values of K_L and q_m were obtained from the plot of $1/q_e$ against $1/C_t$ shown in Figure (5).

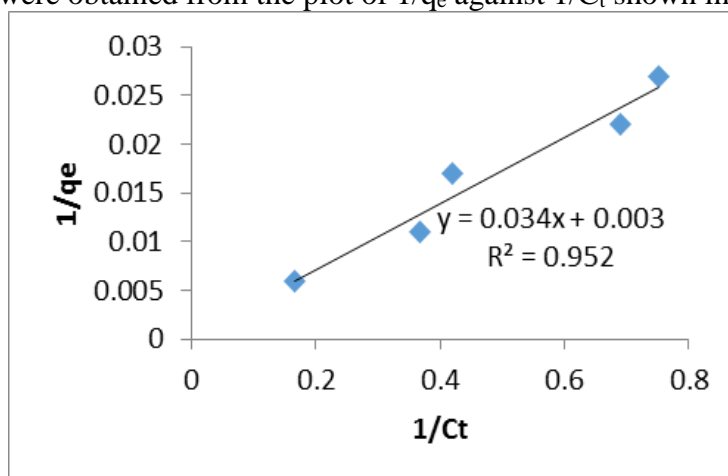


Figure 6: Langmuir adsorption Isotherm for Fe^{2+} adsorption on luffa cylindrical.

The Freundlich isotherm correlation describes adsorption in a non-uniform system (multilayer) and is represented linearly as:

$$\text{Log } q_e = \text{Log } k_f + \frac{1}{n} \text{Log } C_e \quad (5)$$

With k_f and n indicating adsorbent capacity and adsorption intensity (Freundlich constants) respectively. A plot of $\text{Log } q_e$ versus $\text{Log } C_e$ gives a linear graph with slope of $1/n$ and intercept of k_f as shown in Figure(6).

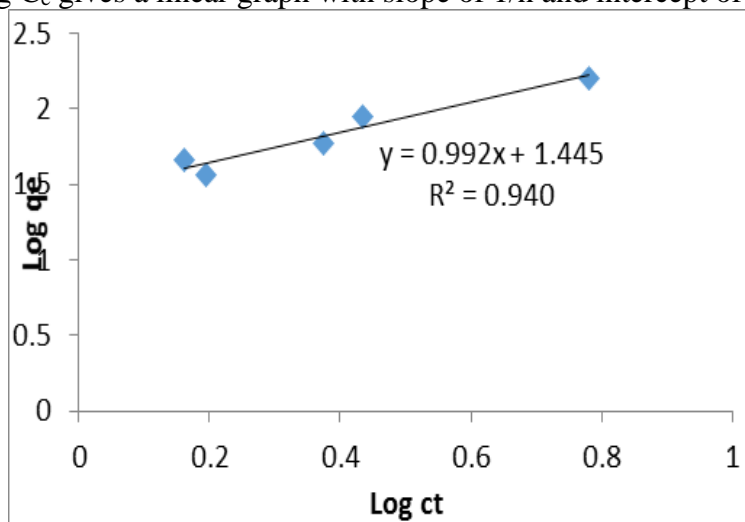


Figure 7: Freundlich adsorption isotherm for iron (II) adsorption on luffa cylindrical.

Table 2: Langmuir and Freundlich parameters for the adsorption of iron (II) on *Luffa cylindrica*

Models	Langmuir constants				Freundlich Constants		
parameters	q_m	K_L	R^2	R_L	k_f	n	R^2
	(mg/g)	(L/mg)			(mg/g)		
Values	333.33	0.088	0.952	0.297	27.86	1.008	0.942

The adsorption isotherm indicates that the experimental results for the adsorption of iron(II) from textile industry effluent were better fitted to Langmuir equation ($R^2=0.952$) as compared to Freundlich equation ($R^2=0.942$), the q_m obtained is in agreement with studies conducted and reported in previously by Abimbola et al[13] and Okolo et al[14].

3.7 Kinetic Model

For the examination of the various mechanisms controlling the process of adsorption (chemical reaction, mass transfer, etc.), Langergren pseudo-first-order and pseudo-second-order correlations were utilized to test the experimental data. The integral from the Langergren pseudo-first-order equation is given as:

$$\text{Log } (q_e - q_t) = \text{Log } q_e - \frac{K_1 t}{2.303} \quad (6)$$

Where q_e is the amount of adsorbed adsorbate on the adsorbent at equilibrium, q_t is the amount of adsorbed adsorbate on the adsorbent at the time, K_1 is the adsorption constant of pseudo-first-order. Figure (7) shows the plot of Langergren pseudo-first-order correlation for the adsorption of iron (II) from the textile industry effluent using *luffa cylindrica* activated carbon. The kinetics parameter for the adsorption process (pseudo-first order rate constant, K_1) can be obtained from the gradient of the plot of $\text{Log } (q_e - q_t)$ against t .

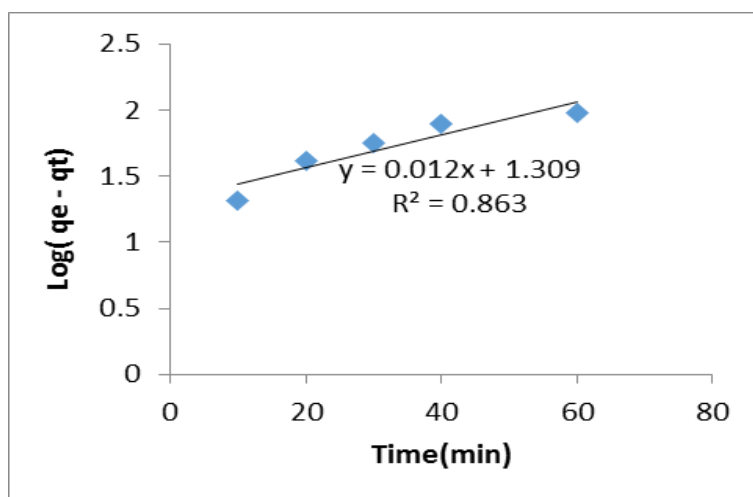


Figure 8: Plot of pseudo-first-order kinetics

For the Langergren pseudo-second-order correlation, the rate depends on the adsorption equilibrium capacity and not on the concentration of the adsorbate and is represented linearly by:

$$t/q_t = 1/h + 1/q_e(t) \quad (7)$$

Where K_2 is the rate of pseudo-second-order, $h = K_2q_e^2$ can be regarded as the initial adsorption rate when $t = 0$, and t represents the time of contact of the adsorbent and the solution. Figure (8) is the plot for the adsorption of metal iron from the textile industry effluent following the pseudo-second-order correlation.

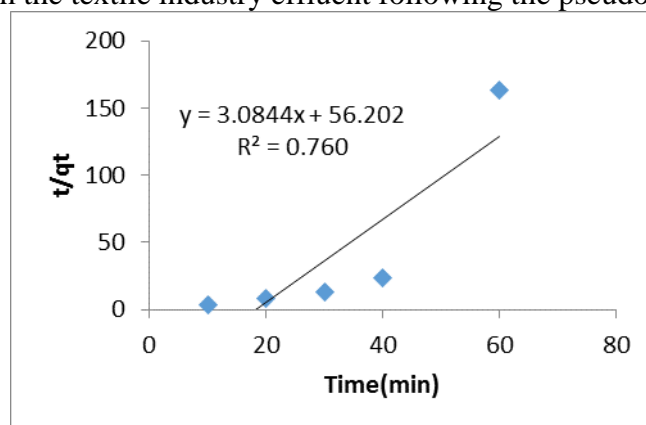


Figure 9: Plot of pseudo-second-order kinetics

Table (3) shows the kinetic parameters for the adsorption of metal iron from the textile industry waste effluent using *luffa cylindrica* activated carbon.

Table 3: Kinetic parameters for pseudo-first and pseudo-second-order for adsorption of iron (II) on *luffa cylindrica*

Metal	Pseudo-first order			Pseudo-second order		
	K_1	q_e	R^2	K_2	q_e	R^2
Iron II	(min^{-1})	(mg/g)		(min^{-1})		
Values	-0.029	20.86	0.863	-0.169	0.324	0.760

4 Conclusion

The present study investigated the removal of iron (II) ions from the textile industry effluent using the activated form of a low-cost adsorbent (*luffa cylindrica*). The uptake of iron (II) ions was found to be affected by contact time of adsorbent with the effluent, pH of the solution, adsorbent dose respectively. The optimum operating parameters were found to be at the time of 60mins and pH of 6. The experimental data obtained from the adsorption experiment were fitted with Langmuir and Freundlich isotherms and the result appeared to be well defined by Langmuir isotherm model indicating monolayer adsorption with regression of correlation of 0.952 as to 0.942 given by Freundlich isotherm model. The kinetic studies indicate conformance with the pseudo-first-order kinetic model, suggesting the tendency rate-determining step involving both the adsorbate and the adsorbent.

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