Parametric Statistical Significance of Iron (II) Ions Adsorption by Coconut Shell in Aqueous Solutions

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Abstract

The parametric statistical adsorption of chemically unmodified Coconut Shell Powder (CSP) to adsorb iron (II) ions from aqueous solutions was examined in this work. It was observed that the adsorption capacity increased with increasing adsorbent dose, reducing adsorbate concentration, increasing contact time, decreasing temperature and reducing particle size. As observed, about 1g of the adsorbent was sufficient enough to remove 98 % iron (II) ions. A total contact time of about 40 minutes was sufficient for almost complete adsorption of the ions, while a pH of about 6.0 exhibited the maximum adsorption capacity. The sorption data was fitted most with the Freundlich Isotherm model with an R^2 value of 0.9719 and standard error of regression value of 0.053. The energy values obtained from the Temkin and Dubinin-Radushkevich isotherm model indicated high chemisorption phenomenon with the adsorbents with values of 485.55 and 2236000.09 $Jmol^{-1}$ respectively. Investigation of some kinetic models confirmed that the adsorption of iron (II) ions using CSP was a pseudo-second order kinetic process, which further corroborates that chemisorption dominates the adsorption. Fourier Transform Analysis (FTIR) further established and justified the outcome of the study. The adsorption was parametrically justified statistically with Analysis of Variance (ANOVA) and Bonferroni-Holm Posthoc significance test. Conclusively, coconut shell proved strongly to be an effective and suitable adsorbent for removing iron (II) ions from aqueous solutions.

Keywords: Coconut, Iron (II), adsorbent, adsorbate, isotherm, kinetics.

Introduction

Iron is present in two major forms in water; the soluble ferrous iron (Fe^{2+}), or the insoluble ferric iron (Fe^{3+}). Ferrous iron in water is a clear and colourless solution, but on exposure to air becomes oxidized to the insoluble reddish brown ferric iron known as rust. Oxidation rate of ferrous to ferric iron seems slow, allowing ferrous iron to remain in aerated water for some time. As a recommendation, iron in drinking water should not exceed 0.3 ppm [1].

At concentrations greater than this limit, iron in aerated water forms significant rust. This rust forms stains on items, gives water a metallic taste and odour, which makes it unpleasant to use. Discoloured water as a result of rust had been identified as the most common complaint about drinking water supply [2]. Iron in water distribution systems causes growth of microorganisms, leading to high contamination [3].

Removal of iron and various metals from solutions by adsorption using agricultural wastes (coconut shell inclusive) regarded as biosorption is widely reported. Tahir and Rauf [4] studied the removal of Fe (II) from wastewater from a galvanized pipe manufacturing industry onto bentonite clay. Parametrically increasing adsorbent dose increased the percentage adsorption of Fe (II). The presence of other metal ions (such as zinc, manganese, lead, cadmium, nickel, cobalt, chromium and copper) reduced the adsorption of iron except zinc. Adsorption capacity up to 98% was achieved at a pH of 3, using an initial 100 mgL^{-1} Fe (II) concentration and 0.5 g of bentonite clay. Over 99 % adsorption of iron was achieved with 5 g of bentonite clay using 0.3 M nitric acid solution for activation. The adsorption followed first order kinetics and fitted the Langmuir and the Freundlich isotherms. In another effort,

Mohana and Chander [5] examined the sorption of iron and manganese on lignite (soft brown coal), with a view to solve the problem of acid mine drainage. Fe (II) sorption increased with increasing pH till about a pH of 7.0. The sorption data correlated very well with both Langmuir and Freundlich isotherms. As reported, adsorption of Fe (II) increased with increasing temperature; at 10 °C, the adsorption of Fe^{2+} was 24.70 mgg^{-1} of lignite, 34.22 mgg^{-1} at 25 °C, and 46.46 mgg^{-1} at 40 °C. The adsorption capacity of lignite in the presence of other metal ions, was found to be higher than most other available adsorbent examined and carbons as reported.

Tariq *et al.* [6] reported the adsorption of copper and iron using pine fruit powder as an adsorbent. Experimental data displayed similar adsorption process for both metals, as the two fitted the Freundlich isotherm. Adsorption capacity of copper ranged from 96.5 to 97.3%, while that of iron was from 94.1 to 97.2 %. The adsorption of both metals followed pseudo-second order kinetics pointing towards chemisorption as the rate determining step in the process. Coconut shells as an adsorbent had been utilised by Beenakumari [7] for the removal of iron from water using Manganese (IV) oxide modified carbon made from coconut shell. The absorbent was effective in removing iron up to 500 ppm concentrations. A decrease in the particle size of the absorbent increased adsorption of the iron, but beyond 0.4 mm, the absorbent became difficult to filter from the system as observed. In the account, an optimum residence time for the removal of iron in water was found to be 4 hours. Ahamad and Jawed [8] investigated the removal of Fe (II) from drinking water with wooden charcoal. The Fe (II) solution was subjected to a treatment with 0.1 M nitric acid. The equilibrium adsorption time was between 150 – 180 minutes. The adsorption followed a pseudo-first order kinetic model; the adsorption mechanism was via surface

adsorption, and intra-particle diffusion. The adsorption fitted the Freundlich adsorption isotherm as observed.

Furthermore, Nieto *et al.* [9] studied the adsorption of iron onto crude stones. Olive stones (a waste in the production of olive oil) was washed, dried and grounded. Adsorption capacity increased with decreasing particle size of the adsorbent as reported. The percentage adsorption of iron increased from 30 to 70% as the crude stone mass increased from 25 to 125 gdm^{-3}. The optimum concentration of adsorbent to adsorbate was reported as 37.5 gdm^{-3}. The adsorption was found to fit the Langmuir isotherm model.

For further investigation, Oyedeji and Osinfade [10] studied the removal of copper (II), iron (III) and lead (II) ions from mono-component simulated waste effluent by adsorption on coconut husk. Unmodified dried and ground coconut husk was used experimentally to study how various operating variables affects adsorption. The adsorption of Fe (III) was reported as maximum at 94 ± 1.4 % at pH range of 5 – 7 and metal ion concentration of 50 ppm. The optimum temperature was given as 50 °C. Maximum contact time of 45 minutes was used for iron adsorption and about 1 g of the adsorbent material was found to be optimally needed for all the metal ions. The Freundlich isotherm was observed to be suitable for the Fe (III) adsorption and the process followed pseudo-second order kinetics.

Radnia *et al.* [11] have also experimentally determined the isotherm and kinetics of Fe (II) adsorption onto Chitosan beads in a batch process. With an adsorbent dose of about 0.15g and a pH of the metal solution of about 4, experiments had been carried out with varying adsorbate concentrations from 10 – 50 mgL^{-1} at 20 °C. The kinetics followed the non-linear pseudo first order, and the experimental data fitted with varying degrees into the Langmuir - Freundlich isotherm model. Kinetic data also revealed that rate of adsorption was dominated by intra-particle diffusion as reported. In another complementary effort, Halnor *et al.* [12] investigated the use of *Syzygium cumini* Leaf Powder (SCLP) as a low cost adsorbent to remove Fe (II) from aqueous solution. Some parameters like concentration of adsorbent and absorbate, contact time, temperature and pH of the solution were varied. The adsorption capacity of SCLP increased by increasing adsorbent dose, reducing the concentration of the adsorbate and increasing the operating temperature up to 40 °C, beyond which adsorption became retarded as observed. The adsorption capacity increased with increasing pH, with a limiting value of 7. A maximum contact time of 50 minutes was needed for the adsorption. The process followed a second order kinetics and fitted the Freundlich isotherm. Thermodynamically Fe (II) adsorption onto SCLP was favourable and spontaneous as informed.

Progressively, Veena *et al* [13] also assessed the effectiveness of activated carbon to adsorb Chromium. Activated carbon was prepared by the pyrolysis of coconut shell in their work. The outcome indicated that the adsorption capacity depends on the surface area and temperature of activation of the activated carbon. Adsorption was reported to be maximum at pH of 3. They concluded that activated carbon is a good adsorbent for the adsorption of chromium from industrial effluents.

Also, Arivoli *et al.* [14] have examined the batch adsorption of Fe (II) from aqueous solution using activated carbon produced from *Strychnos Nux-Vomica L* leaves. It was noted that the adsorption of Fe^{2+} increased with increasing pH, with a limiting value of 6. The equilibrium contact conditions were reported as 60 min, 30 °C, pH of 6.5, while the maximum adsorption of Fe^{2+} was 92.72%. Equilibrium data fitted the Freundlich adsorption isotherm, and the process followed pseudo-second order kinetics. The thermodynamics revealed a negative Gibbs free energy, which indicated the adsorption of Fe^{2+} was spontaneous and feasible.

In another effort, Agbozu and Emoruwa [15] investigated the batch adsorption of heavy metals (Cu, Pb, Fe, Cr, Cd) using coconut husk. Unmodified coconut husk powder was used in batch mode experiments. Adsorption increased with increasing adsorbent dose with about 0.4 - 1.2 g of the coconut husk to 50ml of synthetically prepared waste water. As observed, adsorption trend was in the order of Cr>Cu>Pb>Fe>Cd. Adsorption was also found to increase with increased pH of solution with the trend; Cd>Fe>Cr>Cu> Pb. A maximum contact time of about 20 minutes was required to obtain about 84.9 – 97 % removal of iron from the synthetically prepared waste water. The adsorption reportedly followed the Langmuir isotherm.

In this work, the effects of process parameters such as; temperature, concentration of adsorbate, particle size of the adsorbent, contact time and pH of adsorbate solution on the adsorption capacity of CSP was investigated for better understanding. In addition, the kinetics of the batch adsorption of iron II ions in aqueous solution using CSP with the fitting of the adsorption process to an isotherm model was also investigated for improved operation.

Materials and method

A. Materials
The Adsorbent
Coconut shell was obtained from Badagry, Lagos, Nigeria.

Adsorbent preparation
The adsorbent was prepared using an adaptation of methods described in Oyedeji and Osinfade (2010) with Agbozu, and Emoruwa (2014), which utillised coconut husk for the adsorption of some metallic ions as well as some parametric produres in Olufemi *et al.*, [16]. The coconut shell was washed with water to remove sand and other extraneous materials. It was then sun dried for 3 days, after which it was ground.

The Adsorbate
Ferrous sulfate heptahydrate was used as the adsorbate and was obtained from Finlab, Ikorodu Road, Lagos, Nigeria. The adsorbate was prepared as described in Radnia *et al.* (2011). Stock solution of 1000 mg/L of Fe (II) ions was prepared using crystalline ferrous sulphate heptahydrate salt and distilled water. The stock solution

was diluted with distilled water to give the required concentrations when necessary as required. The following dilution equation was used to calculate required concentrations:

$$C_1 V_1 = C_2 V_2 \qquad (1)$$

where,

C_1 is the initial concentration of adsorbate before dilution (mgL^{-1}), C_2 is the final concentration of adsorbate after dilution (mgL^{-1}), V_1 is the initial adsorbate volume before dilution (L) and V_2 is the final adsorbate volume after dilution (L)

Volume of distilled water to be added $= V_2 - V_1$

Apparatus and Reagents used

Analytical grade Hydrochloric Acid (HCl), Hammer mill (Broyeur Clero), Mesh Sieve (B.S.S. 200 - 100), Electric water bath shaker (Wine light analytical systems OLS 200), Graduated cylinders and beakers (Pyrex, England), Electronic weighing balance (AL Mettler Toledo GmbH), Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer Analyst 200), Electric oven (Gallenkamp, England), Furnace, Funnels, Whatman Filter paper, Electronic pH meter (HANNA Instruments pHep®), Stopwatch, Distilled water, Analytical grade ferrous sulphate hepta-hydrate salt, and Coconut shell.

B. Batch Experimental Procedures

Batch adsorption experiments were conducted in 250 ml beakers using 50 ml of prepared iron solution. The amount of iron (II) ion adsorbed by the coconut shell was determined using,

$$q_i = \frac{C_i V_i - C_f V_f}{m} \qquad (2)$$

where, C_f is the final concentration of adsorbate (mgL^{-1}), C_i is the initial concentration of adsorbate (mgL^{-1}), V_i is the initial adsorbate volume (L) and V_f is the final adsorbate volume (L).

Experiments were carried out at room temperature, except otherwise stated.

Studies on effect of temperature on adsorption of Fe(II) ion

About 400 ml of 100 mgl^{-1} of the iron solution was prepared from the stock solution, using distilled water. Exactly 50 ml of the prepared 100 mgl^{-1} adsorbate was poured into 6 separate 250 ml glass beakers. About 0.20 g of the adsorbent was put into the beakers containing the adsorbate solution. The beaker was placed in a water bath shaker for at a speed of 120 rpm for 20 minutes at 20 °C. This procedure was repeated at temperature range of 20 °C to 70 °C using 10 °C intervals. The adsorbent was filtered using a funnel and filter paper. The filtrate was placed in a

spectrophotometer and the concentrations were measured and recorded.

Studies on the effect of adsorbate dose on adsorption

About 200 ml of 20 mgL^{-1} of adsorbate was prepared using distilled water in a 250 ml beaker. A mass of 0.20 g of the absorbent was introduced into a 50 ml adsorbate solution. The beaker was placed in an electric water bath shaker, using 120 rpm for 20 minutes. This procedure was repeated at various adsorbate concentration using 40 mgl^{-1} to 100 mgL^{-1} with 20 mgL^{-1} intervals. The adsorbent was filtered using a funnel and filter paper. The filtrate was later placed in a spectrophotometer and the concentrations measured and recorded.

Studies on the effect of adsorbent dose on adsorption

A volume of 300 ml of 100 mgL^{-1} adsorbate was prepared using distilled water in a 250 ml beaker. About 50ml of the prepared adsorbate was poured into five separate beakers. Measured 0.20 g of the absorbent was put into one of the beakers containing the adsorbate solution. The beaker was placed in an electric water bath shaker at 120 rpm for 20 minutes. This procedure was repeated with varying adsorbent dose from 0.40 g to 1.0 g using 0.2 g intervals. The adsorbent was filtered using a funnel and filter paper, the filtrate was put in a spectrophotometer and the concentration measured and recorded.

Studies on the effect of contact time on adsorption

Exactly 50 ml of the prepared 100 mgL^{-1} adsorbate was poured into 5 separate glass beakers. About 0.50 g of the adsorbent was placed into the beaker containing the adsorbate. The beaker was placed in an electric water bath shaker at 120 rpm for 20 minutes. This procedure was repeated at various contact time from 20 to 120 minutes using 15 minutes intervals. The adsorbent was filtered using a funnel and a filter paper. The filtrate was put in a spectrophotometer and the concentration values measured and recorded.

Studies on the effect of particle size on adsorption

About 50 ml of the prepared 100 mgL^{-1} adsorbate was poured into 5 separate glass beakers. A quantity of about 0.20 g of the adsorbent was put into the beaker containing the adsorbate. The beaker was placed in an electric water bath shaker at 120 rpm for 20 minutes. This procedure was repeated using a various particle sizes of 75 – 150 microns. The adsorbent was filtered using a funnel and filter paper. The filtrate was put in a spectrophotometer and the concentrations measured and recorded.

Studies on the effect of pH on adsorption

Fifty millilitres of the prepared 100 mgL^{-1} adsorbate was poured into 5 separate glass beakers. The pH of the solution

was adjusted to 1.0 using 1 M HCl solution. The beaker was placed in an electric water bath shaker at 120 rpm for 20 minutes. This procedure was repeated varying the pH of the solution from 2.0 to 14.0 by adding either 1 M HCl or 1 M NaOH solution. The adsorbent was filtered using a funnel and filter paper. The filtrate was put in a spectrophotometer and the concentrations measured and recorded accordingly.

Results and discussions

A.   Characterization of the Adsorbent

Table 1 presents the physical properties of the adsorbent with values of the specific gravity, porosity, moisture content and bulk density.

Table 1:   Physical Properties of the Coconut Shell Adsorbent

Property	Value
Moisture content (%)	4.90
Bulk density (gcm^{-3})	0.67
Specific Gravity	1.42
Porosity	0.53

B.   Effect of Process Parameters on Adsorption Capacity

From Fig. 1, it can be seen that the removal of 50 ml of 100 mg/L adsorbate increased as adsorbent dose was increased from 0.2 g till about 0.8 g.
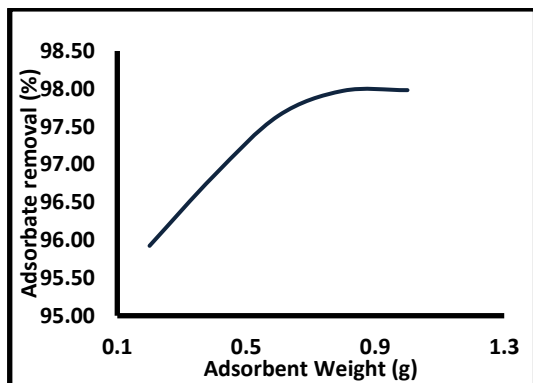

Fig. 1: Effect of Adsorbent Dose on Adsorption of Iron (II) at an Adsorbate Dose of 50 ml of 100 mgL^{-1}, Adsorbent Particle Size of 75 µm, Shaking Time of 20 minutes, Shaking Speed of 120 rpm and Temperature of 27 °C.
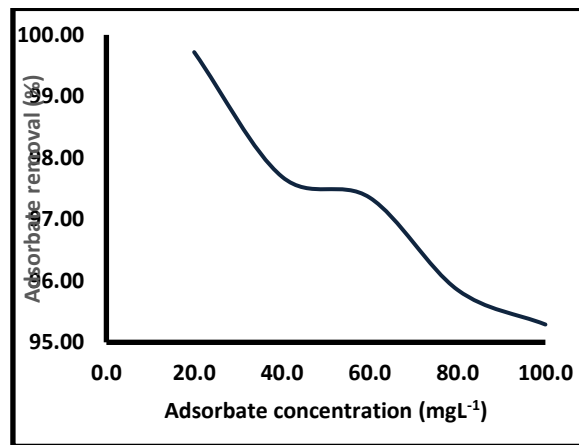

Fig. 2: Effect of Adsorbate Dose on Adsorption of Iron (II) at an Adsorbent dose of 0.2 g, Adsorbent Particle Size of 75 µm, Shaking Time of 20 minutes, Shaking Speed of 120 rpm and Temperature of 27 °C.

Percentage removal remained constant with an adsorbent dosage of 1.0 g suggesting that 0.8 g of the coconut shell powder is sufficient to remove Iron (II) ions and the maximum removal of iron was 98%.

As shown in Fig. 2 above, removal of Iron (II) ions decreased from 99.7% to 95.2% as the adsorbate concentration increased from 20 mg/L to 100 mg/L. This indicated that increasing the adsorbate concentration causes a decrease in the adsorbate percent removal.
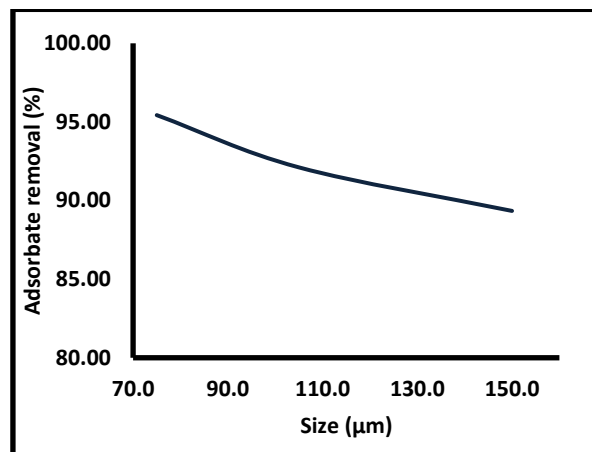

Fig.3: Effect of Particle Size of Adsorbent on Adsorption of Iron (II) at an Adsorbate Dose of 50 ml of 100 mgL^{-1}, Adsorbent Dose of 0.2 g, Shaking Time of 20 minutes, Shaking Speed of 120 rpm and Temperature of 27 °C

As plotted above in Fig. 3, the removal of iron using coconut shell dropped from 95 % to 89 % as the particle size of the coconut shell increased from 75 to 150µm. A reduction in particle size translates to an increase in surface area of the adsorbents, meaning that more active sites are available for adsorption than before.
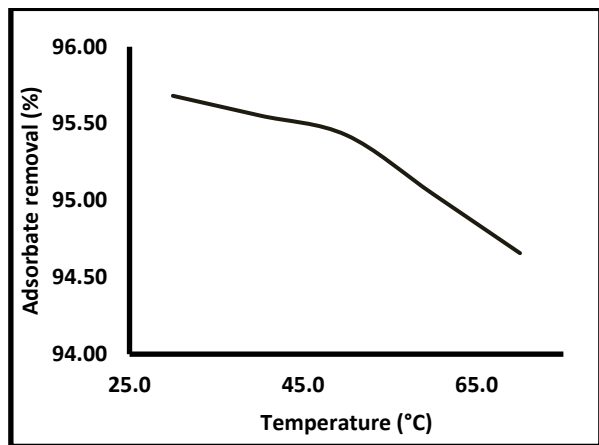
Fig. 4: Effect of Temperature on Adsorption of Iron (II) at an Adsorbate Dose of 50 ml of 100 mgL^{-1}, Adsorbent Dose of 0.2 g, Adsorbent Particle Size of 75 µm, Shaking Time of 20 minutes and Shaking Speed of 120 rpm.

The percentage removal of iron dropped from 95.7 % at 30 °C to 94.6 % at 70 °C as shown in Fig. 4. For all adsorbents used, the adsorption efficiency drops with increase in temperature from 20 °C to 70 °C. One can easily say this is characteristic of physisorption as observed also by Santuraki et al. [17] with similar trend.
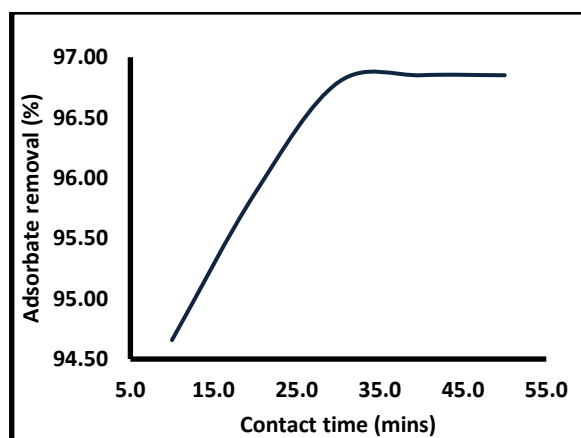

Fig. 5: Effect of Contact Time on Adsorption of Iron (II) at an Adsorbate Dose of 50 ml of 100 mgL^{-1}, Adsorbent Dose of 0.2 g, Adsorbent Particle Size of 75 µm, Shaking Speed of 120 rpm and Temperature of 27 °C.

An important parameter that affects the adsorption capacity of an adsorbent-adsorbate system is the contact time. Higher contact time means that more active sites on the surface of the adsorbent can be occupied with the adsorbate, till saturation and no more adsorption can occur. This is seen in Figure 3.4 above as the removal of iron increased from 94.5 % to 96.8 % as contact time increased from 10 to 40 mins, after which it remains constant. This implied that after 40 minutes the adsorbent was completely saturated with Iron (II) ions and no more adsorption occurred.
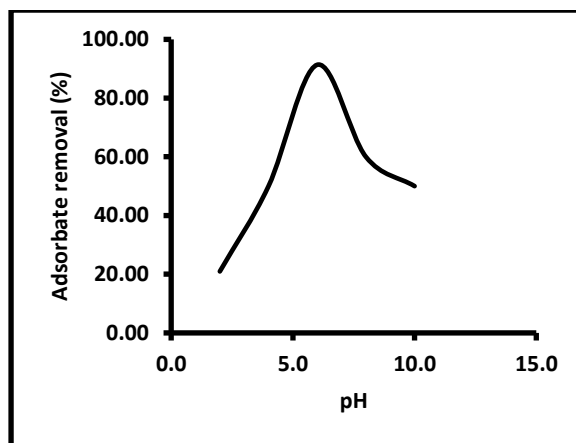

Fig. 6: Effect of pH on Adsorption of Iron (II) at an Adsorbate Dose of 50 ml of 100 mgL^{-1}, Adsorbent Dose of 0.2 g, Adsorbent Particle Size of 75 µm, Shaking Speed of 120 rpm and Temperature of 27 °C.

As shown in Fig. 6, the adsorbate removal increases from 20.95% at a pH of 2 to 91.35% at a pH of 6, after which it dropped to 46.09% at a pH of 11. At the neutral pH of 7, adsorption removal was 78%. The adsorption capacity of coconut shell powder decreases as the adsorption system becomes either more acidic or alkaline, with a noticeable steeper range in the acidic region. This phenomenon could be partially explained by the observation proposed by Agbozu and Emoruwa [15] that lower pH values furnishes more H$^+$ ions that competes with the adsorption active sites with Fe^{2+} ions. However, with the observation in Figure 3.6, a higher alkaline pH value also has the capability of furnishing more OH$^-$ ions which also competes the active sites with Fe^{2+} ions. The H$^+$ ions, seems to pose a more serious threat than OH$^-$ ions, which makes the acidic range slope steeper. Adsorption capability was therefore highest at a pH value of 6.0, which is almost neutral but slightly acidic.

C. Fourier Transform Infrared Spectroscopy (FTIR) Analysis of Adsorbents

The FTIR analysis shows the functional groups present. The FTIR spectroscopy of the coconut shell powder before and after adsorption is shown in Fig. 7. After adsorption, the residue is seen to have water as indicated by the OH$^-$ and Fe^{2+} peak in the FTIR chart, compared to the dry coconut shell powder that contained no ion before adsorption. This showed that adsorption occurred.
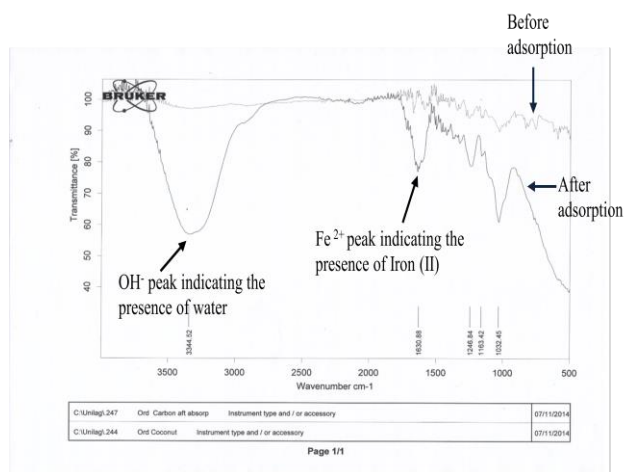
Fig. 7: The FTIR Spectroscopy showing Functional Groups in Ordinary Coconut Shell before and after Adsorption at an Adsorbate Dose of 50 ml of 100 mgL^{-1}, Adsorbent Dose of 0.2 g, Adsorbent Particle size of 75μm, Shaking Speed of 120 rpm, Shaking Time of 20 minutes and Temperature of 27 °C.

D.   Adsorption Isotherms

Some review of literature on the adsorption of Fe(II) ions using chemically unmodified adsorbents like saw dust, lignite, bentonite clay, olive stones and so on reveals that the adsorption of Fe(II) ions fits into Langmuir isotherm but follows Freundlich isotherms with carbon and activated carbon made from these adsorbents.

In Table 2, for the Coconut shell, the maximum saturation capacity Q_O was 204.0816 mg of Iron (II) ions to 1 g of ordinary coconut powder for shaking done for 20 minutes at 120 rpm. Its Langmuir isotherm constant was obtained as 0.1756 Lmg^{-1}. The less than one R_L value indicates favourable adsorption, while a value of zero indicates an irreversible adsorption. Therefore, adsorption of Iron (II) ions at $R_L = 0.0539$ using coconut shell is favourable and almost irreversible. The standard error of regression S, highest error of prediction ε_H and the lowest error of prediction ε_L as given in Table 2 showed that the errors involved in the estimations are minute.

In the Freundlich isotherm, the R^2 values compared to that of Langmuir indicates that the adsorption process fits more into the Freundlich Isotherm as shown in Table 2, supported by the error estimation criteria. The 'n' value indicates homogenous adsorption.

The Temkin isotherm in Table 2 showed that the heat of adsorption decreased with increasing coverage or adsorption of the adsorbate on the adsorbent. The table shows a high equilibrium binding constant of 1.6620 Lg^{-1}. The error estimation was quite high.

This Dubinin-Raduskevich sotherm in Table 2 gives an idea of the mean free energy of adsorption. Value of the mean free energy (E) at 2236.0680 $kJmol^{-1}$ which is greater than 20 $kJmol^{-1}$, suggests that chemisorption occurred. The error estimation was not too high.

TABLE 2: Isotherm Constants

Parameters	Values
Langmuir	
R^2	0.9315
Q_O (mgg^{-1})	204.0816
K_L (Lmg^{-1})	0.1756
R_L	0.0539
S	0 gmg^{-1}
ε_H	+0.20 gmg^{-1}
ε_L	-0.15 gmg^{-1}
Freundlich	
R^2	0.9719
k_a	26.9631
N	0.4953
S	0.053
ε_H	+0.042
ε_L	-0.051
Temkin	
R^2	0.9236
B ($Jmol^{-1}$)	485.5500
A_T (Lg^{-1})	1.6620
S	49.33 mgg^{-1}
ε_H	+44.17 mgg^{-1}
ε_L	-67.88 mgg^{-1}
Dubinin-Radushkevich	
R^2	0.8799
k (mol^2kJ^{-2})	2E-07
E ($kJmol^{-1}$)	2236.0680
Q_s(mgg^{-1})	447.6448
S	0.0018
ε_H	+6.16
ε_L	+6.15

E.   Adsorption Kinetics

Comparing the values of the coefficient of correlation (R^2) and error estimation criteria in Table 3, it can be seen that the adsorption of iron (II) ions fitted perfectly into the Pseudo Second Order kinetic model. With the maximum monolayer coverage of the adsorbent estimated at 476.1905 mgg^{-1} of the coconut shell powder and the pseudo second order constant of 0.0074 g mg^{-1} min^{-1}.

The Pseudo Second Order kinetic model is based on the assumption that chemisorption controls the rate of adsorption, and chemisorption is considered irreversible. The error estimates of the pseudo-second order kinetics was small enough to validate the authenticity of the model with a standard error of regression value of 0.0001 $min.gmg^{-1}$

q_e (mgg^{-1})	476.1905
k_2 (g mg^{-1} min^{-1})	0.0074
S	0.0001 min.gmg^{-1}
ε_H	-0.002 min.gmg^{-1}
ε_L	-0.00047 min.gmg^{-1}
Intra-particle Diffusion	
R^2	0.6450
k_{id} (mg g^{-1} min$^{-1/2}$)	85.1880
S	114.07 mgg^{-1}
ε_H	+203.9 mgg^{-1}
ε_L	-118.16 mgg^{-1}

Table 3: Kinetics Constants

Parameters	Values
Pseudo-First Order	
R^2	0.9073
k_1 (min^{-1})	0.1817
q_e (mgg^{-1})	94.3301
S	0.82
ε_H	+0.67
ε_L	-0.33
Pseudo-Second Order	
R^2	1.0000

Table 4: Analysis of Variance (ANOVA) and Bonferroni-Holm Posthoc Significance Test for Iton (II) ions Adsorption by Coconut Shell with varying Parameters

Group1	Group2	Analysis of Variance (ANOVA) Test						Bonferroni-Holm Posthoc Significance		
		S_{SB}	S_{SW}	D_{FB}	D_{FW}	F	P	P_C	P	Significant
W_A	P_R	23365.24	3.528083	1	8	52981.15	1.42E-16	0.05	1.42E-16	Yes
C_f	P_R	3456.067	4012.079	1	8	6.891324	0.030407	0.05	0.030407	Yes
S_P	P_R	15444.9	18955.7	1	8	6.518315	0.03401	0.05	0.03401	Yes
T	P_R	300	3500	1	10	0.857143	0.376342	0.05	0.376342	No
t	P_R	4000	2000	1	8	16	0.00395	0.05	0.00395	Yes
pH	P_R	7178.892	1190.617	1	7	42.2069	0.000335	0.05	0.000335	Yes

The ANOVA and Bonferroni-Holm Posthoc significance test for iron (II) ions adsorption by coconut shell with varying parameters is given in Table 4. The statistical computation presented were carried out with the aid of Daniel's XL Toolbox Version 6.70 © 2008 - 2013 software. The parameters investigated showed the actual values of the sum of squares within the groups and the sum of squares between the groups. There existed a statistically wide variation between the individually investigated parameters and the equilibrium concentration groups at the 95% confidence interval, as the $F(D_{FB}, D_{FW})$ and P values are mostly within expected ranges. Fisher's F is a ratio of the variance between groups to the variance within groups and P is a probability factor that must be less than 0.05 in the ANOVA analysis. The degree of freedom between the groups was 1, while the degree of freedom within the groups was between 7 to 10. The F and P values implied a strong dependence of P_R on most of the parameters investigated (W_A, C_f, S_P, t, and pH). The Bonferroni-Holm Posthoc parametric significance test for various parameters investigated showed a strong dependence or significance on each other except for the relationship between P_R and T with a P value of 0.376342 which was greater than 0.05 in the 95% confidence interval.

Conclusions

From the results, it is seen that the adsorption capacity of the Coconut shell powder indicated by the removal of Iron(II) ions increases with increasing adsorbent dose, reducing adsorbate dose, increasing contact time, decreasing temperature and reducing particle size.

As observed, 1 g of the adsorbent seems to be sufficient for treating 50 ml of 100 mgL^{-1} of the Iron (II) solution, with a maximum achievable removal of 98 %. This percentage removal is an improvement over that of Agbozu and Emoruwa [15] with a maximum removal of 97%. A total contact time of about 40 minutes was found to be appropriate for the complete adsorption of the ions. In addition, highest adsorption capacity was obtained at a pH value of 6.0, indicating preference for a slightly acidic environment..

The adsorption of Iron (II) ions using coconut shell powder followed the Freundlich Isotherm model. It also fitted perfectly into the Pseudo-Second Order Kinetic model. This indicated as corroborated by the high energy values obtained from the Dubinin-Radushkevish isotherm model that Chemisorption controls the adsorption process.

From the outcome so far, it can be concluded that a waste material like Coconut Shell Powder (CSP) is an effective and suitable adsorbent for removing Iron (II) ion from aqueous solution, and a probable cost effective adsorbent for treating Iron (II) contaminated water. Furthermore, the adsorption was justified statistically using ANOVA and Bonferroni-Holm Posthoc significance test, which confirmed the strong importance of process parameters as implemented also in the adsorption of nickel (II) ions with banana peel and coconut shell [18].

Nomenclature

A_T Temkin Isotherm Equilibrium Binding Constant (Lg^{-1})

B Temkin isotherm constant $(Jmol^{-1})$

C_1 Initial concentration of adsorbate before dilution (mgL^{-1})

C_2 Final concentration of adsorbate after dilution (mgL^{-1})

C_e Equilibrium concentration of adsorbate (mgL^{-1})

C_f Final concentration of adsorbate (mgL^{-1})

C_i Initial concentration of adsorbate (mgL^{-1})

D_{FB} Degrees of freedom between groups

D_{FW} Degrees of freedom within groups

E Mean free energy of adsorption $(kJmol^{-1})$

ε_H Highest error of prediction

ε_L Lowest error of prediction

F Fisher's ratio

k_a Freundlich Isotherm Constant (mgg^{-1})

K_{ads} Dubinin-Radushkevich isotherm constant (mol^2kJ^{-2})

k_{id} Intra particle diffusion rate constant $(mg\ g^{-1}\ min^{-1/2})$

K_L Langmuir isotherm constant (Lmg^{-1})

k_1 Pseudo-first order rate constant (min^{-1})

k_2 Pseudo-second order rate constant $(g\ mg^{-1}\ min^{-1})$

m Mass of adsorbent (g)

n Freundlich Isotherm Constant

P probability factor

P_C Critical probability factor

pH   Level of acidity or alkalinity

P_R Percent Removal

q_e Amount of metal adsorbed per gram of adsorbent at equilibrium (mgg^{-1})

Q_O Maximum monolayer coverage capacity (mgg^{-1})

q_s Theoretical isotherm saturation capacity (mgg^{-1})

q_t Amount of metal adsorbed per gram of adsorbent any time t (mgg^{-1})

R Universal constant $(8.314\ kJmol^{-1}K^{-1})$

R_L Langmuir Isotherm Separation Factor

R^2 Coefficient of correlation

S   Standard error of regression

S_P Particle Size (μm or microns)

S_{SB} Sum of squares between groups

S_{SW} Sum of squares within groups

t Time (min)

T Temperature (K)

V_1 Initial adsorbate volume before dilution (L)

V_2 Final adsorbate volume after dilution (L)

V_i Initial adsorbate volume (L)

V_f Final adsorbate volume (L)

W_A Adsorbent Weight (g)

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