



Adsorption Isotherm and Kinetics for the Removal of Fe³⁺ from Aqueous Solution using Activated Coconut Wastes

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Abstract This study seeks to investigate the equilibrium and kinetic studies of Fe³⁺ ion adsorption from aqueous solution of 0.05M H₃PO₄ by low cost adsorbents. The adsorbents used were activated coconut shell and coconut coir. The experimental results were fitted to the Langmuir, Freundlich and Temkin isotherms to obtain the measured sorption data. The Kinetics of the process was also measured using the First-order, Second-order and Elovich rate models. Equilibrium studies showed that coconut shell had the highest adsorption capacity. Langmuir and Freundlich models gave the best fit for the experimental data. The kinetic data for the adsorption process obeyed the Elovich rate Equation.

Keywords Adsorption; Isotherm; Iron (III) ion; Removal Efficiency; aqueous solution

Introduction

Industrial waste constitutes the major source of various kinds of metal pollution in natural water [20], [24]. Disposal of agricultural by-product is currently a major economic and ecological issue and the conversion of these agro-products to adsorbent such as activated carbon rather than outright combustion provides a more economically viable alternative in our waste management process [21]. One of the raw materials that has been found to be useful in this process is the coconut waste (shell and coir).

Some of the components of Coconut Palm (*coco nucifera*) are Coconut shell and coir (fibrous material). These materials are composed of several constituents among which are lignin acid and cellulose which bear various polar functional groups including the carboxylic and phenolic acid groups. These materials also find useful application in metal binding, [15]. Coconut shell is an agricultural based waste material and has the capacity to remove metal ions from solution [8]. These materials are present in abundance with high biosorption capacity, cost effectiveness and renewability and also a viable economic alternative for water treatment and waste remediation [1]. The activated carbon prepared from coconut shell and coir is a cheap non-polar and highly porous amorphous solid consisting of micro crystallites with a graphite lattice [2], [11]. The potential of coconut shell and coir to function as biosorbent materials is due to their high content of lignum (35-45%), and cellulose (23-43%) [3], [6], [24]. The cellulose and lignum are biopolymers admittedly associated with the removal of heavy metals [7]. Heavy metal contamination of industrial effluents is one of the significant environmental problems due to their toxic nature and accumulation throughout the food chain as non-biodegradable pollutants [8]. The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment.

As a result of increased industrial activities (mining operations, refining ores, sludge disposal etc), many heavy metals like Iron (Fe), copper (Cu), Lead (Pb), Chromium (Cr), Zinc (Zn), Silver (Ag) etc; are released into the environment [4], [14]. Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great environmental threat worldwide, this is because heavy metals are not biodegradable and have increasing significance owing to their harmful effect on human physiologies and other



biological systems when they exceed the tolerance levels [16], [20]. Adsorption is an effective purification and separation technique used in water and waste water treatment by allowing the collection of a substance onto the surface of adsorbent solids [19].

Materials and Method

The ripe (brown-husk) coconut fruits (*coco nucifera*) from a mature tree of about five years old with an average weight of about 1.3kg per fruit were sourced from a compound in Agbor (Delta State, Nigeria). The shell and the coir were extracted and properly washed with water, air-dried first before they were subjected to oven-drying for about 12 hours at a temperature of 80 °C.

Carbonization was carried out using a muffle furnace which allowed limited supply of air. The washed sun-dried coconut shell and coir were carbonized in the furnace for 3 hours at 550°C after which the products were allowed to cool at room temperature. The cooled product was then pulverized with a manual blender.

Sieve analysis was performed using the sieve screen (Shaker) to obtain final sample particle size of 250 μ m. 25.0 \pm 0.01g of the screened (250 μ m) fine unmodified carbonized shell (UCS) and the unmodified coconut coir (UCC) were carefully weighed out and put in two different beakers containing excess 500 ml of 0.05M H_3PO_4 (aq).

The contents of each beaker were thoroughly mixed and heated on a hot plate until it was turned to a paste. The paste was further dewatered using a Whatman filter paper (No.541) and transferred into a crucible and subsequently subjected to heating in a furnace at a temperature of about 550°C for 2 hours. After cooling the activated sample (adsorbent) at room temperature, it was then washed with water at a P^H of 5.5 and dried on the hot plate at 100°C for about 3 hours.

The treatment of the adsorbent with 0.05M H_3PO_4 solution aided the removal of any debris or soluble bimolecules that might interact with the metal ions during the adsorption process and to open the micro pores of the adsorbent thereby making then ready for adsorption. The activated coconut Shell (ACS) and activated coconut coir (ACC) were labeled accordingly.

Experimental Procedures

Equilibrium adsorption studies were carried out according to the procedure used in the sorption of copper ion from aqueous solution [9], [6], The standard solutions (stock) of each of the metal ions were prepared at a P^H of 5.03 and temperature of 30 °C. From the stock solution, various initial concentrations (10, 20, 30,40,50,60 mg/l) of the metal ions were prepared by serial dilution. 100ml of each solution was transferred into 250ml conical flask, corked and labeled. Thereafter, 2g of each of the adsorbents was weighed into the different flasks and agitated in a shaker for one hour to attain proper mixing and attainment of equilibrium. After the equilibrium time the content of each flask was then filtered using Whatman filter (No. 541) paper and the residue (equilibrium) concentration of each metal ion determined using atomic adsorption spectrometer, AAS. Blank solutions were also prepared for use in the AAS machine calibration. The difference in the concentration of the metal ions before and after adsorption gives the amount of metal ion adsorbed by each adsorbent. Blank solutions were also prepared and analyzed. The mean adsorption capacity, q_e (in mg/g biomass) of these determinations was evaluated from the initial metal ion concentration C_o (mg/l) and final equilibrium concentration C_e (mg/l) in every sample as follows:

$$q_e = (C_o - C_e) \frac{V}{M} \quad (1)$$

Where V is the volume of initial metal ion solution (ml) and M is dry mass of the adsorbent used (g). The removal efficiency RE, (percentage uptake) was also calculated using the equation:

$$RE(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Kinetic adsorption studies were carried out according to the method used in the adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes



[5]. The study was performed for each of the metal ions at P^H of 5.03, temperatures of 30°C and an initial concentration of 50mg/l . 100ml of standard solutions of each metal ion was transferred into different 250ml conical flasks corked and labeled. Thereafter 2g of each of the adsorbents was weighed out and put into the different flasks and agitated at different contact times ($20, 40, 60, 80, 100, 120$ minutes). At the end of agitation time, the content of each flask was centrifuged, filtered and the residual concentration of each of the metal ions analyzed using Atomic Adsorption Spectrometer, AAS.

Results and Discussion

Equilibrium Adsorption Isotherm Models

The capacity of the adsorption isotherm is fundamental and plays an important role in the determination of the maximum capacity of adsorption.

In order to adapt to the system under consideration, the following models were deemed adequate to analyze the experimental results obtained [13], [22].

$$\text{Langmuir model, } q_e = \frac{K_L b C_e}{(1 + K_L C_e)} \quad (3)$$

$$\text{Freundlich model, } q_e = K_f C_e^{1/n} \quad (4)$$

$$\text{Temkin model, } q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \quad (5)$$

Where $R \Rightarrow$ universal gas constant (8.3143J/mol/K), T is the absolute temperature (K), b_T and k_t are the Temkin isotherm constants (L/mol) while q_e and C_e retain their usual meanings, q_e the sorption capacity and C_e , the equilibrium concentration of the metal ion in the aqueous solution.

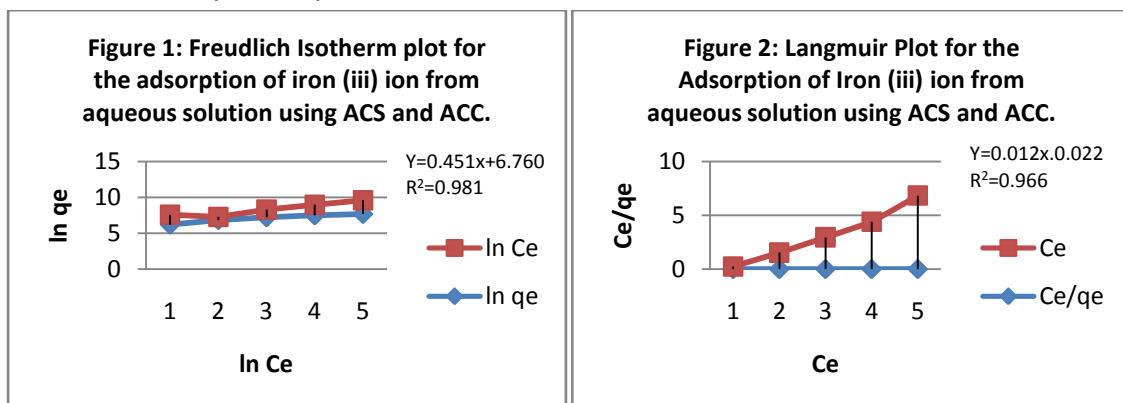
The relationships among q_e , C_e (sorption capacity (q_e) and the aqueous metal ion concentration at equilibrium (C_e) with time as expressed in the equations of Freundlich, Langmuir and Temkin have been examined and plotted as shown in Figures 1, 2 and 3. Analysis of the metal sorption on the adsorbents as described by the three isotherms using coefficient of determination (R^2) value which showed that the Freundlich best describes the sorption of Fe^{3+} on ACS and Langmuir isotherm best describes that of the ACC.

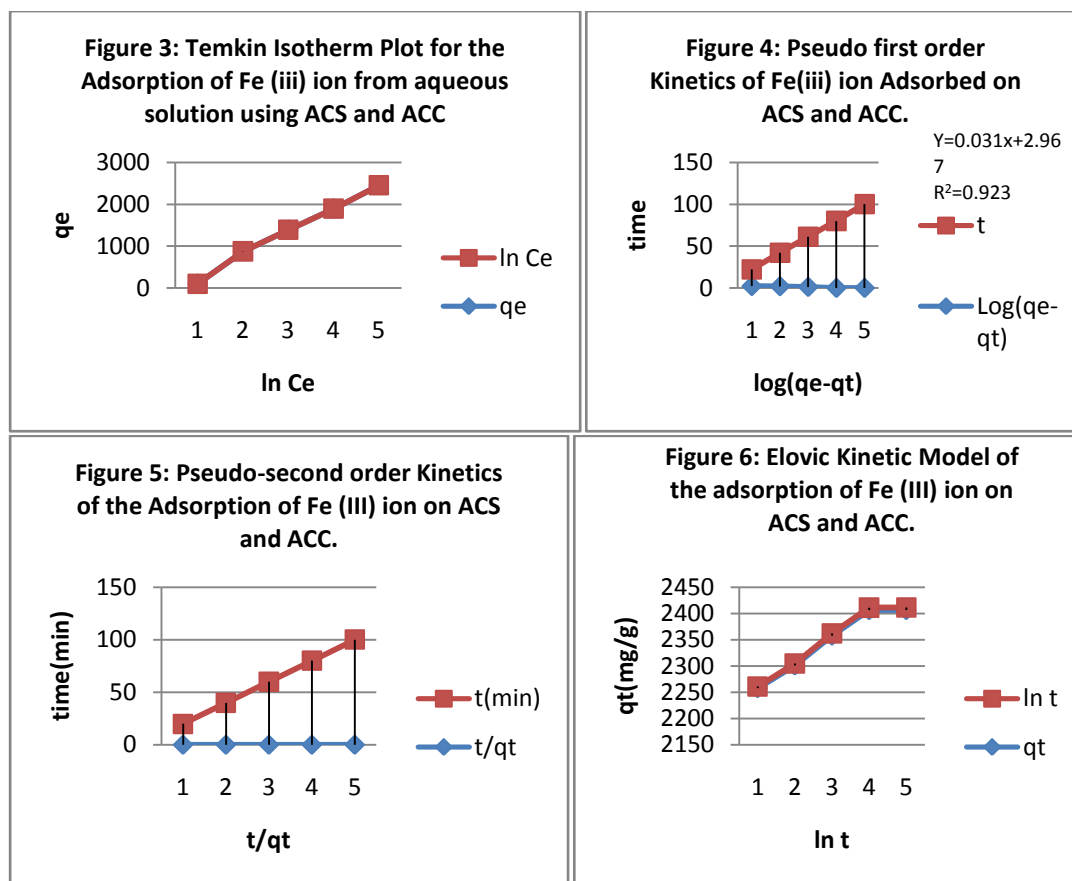
Adsorption Kinetic Models

$$\text{Pseudo first order model, } \log(q_e - q_t) = \log(q_e) - \frac{K_1 t}{2.303}$$

$$\text{Pseudo second order model, } \frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$$

$$\text{Elovich model, } q_t = \frac{1}{\beta} \ln t + \frac{1}{\beta} \ln(\alpha\beta)$$





The kinetic studies of the adsorption of Fe^{3+} to coconut shell and coir were carried out using the Pseudo first order, Pseudo second order and Elovich models on experimental data as shown on the plots (Figures 4,5 and 6). It was therefore observed that the regression coefficients obtained from the pseudo first order kinetic graph were quite low. This implies non-applicability of the pseudo first order kinetic model to the experimental data of the adsorption of Fe^{3+} to coconut shell and coir.

On applying the second order kinetic model by plotting t/q_t against t , high values of regression correlation coefficients were obtained as seen in Figure 5. However their k^2 and q_e values were zero implying that the mechanism of adsorption of Fe^{3+} ions on coconut shell and coir did not also followed the second order kinetics. From Figure 6, the correlation coefficients showed good linearity. It can also be observed that Elovich model gives us an account of the desorption process taking place. It can be seen from the appendix that 'as the initial concentration was increasing, desorption (β) was decreasing in other words initial adsorption (α) was increasing. This suggests that the rate limiting step of iron onto coconut shell and coir may be chemisorptions [9]. Elovich Model (Figure 6), best describes the sorption of the Fe^{3+} by the adsorbents ACS and ACC.

Appendix: Isotherm and Kinetic Studies

Table 1a: Concentrations (Shell)

Co (Mg/L)	Ce (Mg/L)	Qe (Mg/g)	InCe	In qe	Ce/qe(g/L)	%
10	0.248	487.60	1.394	6.189	0.00051	97.52
20	1.53	923.50	0.425	6.828	0.00166	92.35
30	2.95	1352.35	1.083	7.210	0.00218	90.16
40	4.39	1780.60	1.479	7.485	0.00246	89.03
50	6.82	2159.15	1.919	7.677	0.00316	86.37

Where $V=100\text{ml}$ and $M=2\text{g}$.



Table 1b: Concentrations (Coir)

Co(Mg/L)	Ce(Mg/L)	qe(Mg/g)	InCe	lnqe	Ce/qe(g/L)	%RE
10	7.996	100.200	2.079	4.607	0.07980	20.040
20	2.480	876.000	0.908	6.775	0.00283	87.600
30	2.204	1389.800	0.790	7.237	0.00159	92.653
40	2.101	1894.950	0.742	7.547	0.00111	94.748
50	0.994	2450.300	-0.006	7.804	0.00041	98.012

Table 2a: Time (Shell)

Time (t) (min)	Co (Mg/L)	Ce (Mg/L)	Qt (Mg/g)	qe-qt (Mg/g)	Log (qe-qt)	t/qt	Int	logt	%RE.
20	50	5.114	2244.300	153.450	2.186	0.009	2.996	1.301	89.772
40	50	3.909	2304.550	93.200	1.969	0.017	3.689	1.602	92.182
60	50	2.34	2383.000	14.750	1.169	0.025	4.094	1.778	95.320
80	50	2.045	2397.750	0.000	1.000	0.033	4.382	1.903	95.910
100	50	2.045	2397.750	0.000	1.000	0.042	4.605	2.000	95.910

Table 2b: Time (Coir)

Time (t) (min)	Co (Mg/L)	Ce (Mg/L)	Qt (Mg/g)	qe-qt (Mg/g)	Log (qe-qt)	t/qt	Int	logt	%RE.
20	50	4.844	2257.800	148.700	2.172	0.009	2.996	1.301	90.312
40	50	3.98	2301.000	105.500	2.023	0.017	3.689	1.602	92.040
60	50	2.846	2357.700	48.800	1.688	0.025	4.094	1.778	94.308
80	50	1.87	2406.500	0.000	1.000	0.033	4.382	1.903	96.260
100	50	1.87	2406.500	0.000	1.000	0.042	4.605	2.000	96.260

Table 3: Calculated values of the various Isotherm Model parameters

Sample	Freundlich			Langmuir			Temkin		
	n	K _F	R ²	q _m	K _L	R ²	b _j	K _T	R ²
Shell	2.22	862.64	0.981	0.000	0.000	0.912	5.115	7.881	0.890
Coir	-1.629	3881.59	0.908	83.33	-3787	0.966	-2.173	0.125	0.887

Table 4: Values of the Kinetic Model Constants

Model	Pseudo 1 st order			Pseudo 2 nd order			Elovich		
	Ki (L/min)	q _e (mg/g)	R ²	K ₂ (g/mg.min)	(mg/g)q _e	R ²	a (mg/g.min ⁻¹)	P (g/mg)	R ²
Shell	0.0714	1221.80	0.855	0.000	0.000	0.999	23.073	9.89	0.953
Coir	0.714	926.83	0.923	0.000	0.000	0.999	10.232	9.53	0.946

Conclusion

This study was conducted to investigate the isotherm and kinetics for the sorption of Fe³⁺ ion from metal solutions using modified agricultural by-products of coconut shell and coir. Acid activation of the adsorbents might have caused some modification in the adsorbent surface. The results obtained showed that both chemically modified (with orthophosphoric acid) coconut coir and shell are efficient adsorbents for the removal of Fe³⁺ ion from aqueous solutions. Equilibrium data were fitted with the Freundlich, Langmuir and Temkin isotherm models for the system. It was found that the ACS obeyed the Freundlich isotherm while the ACC obeyed the Langmuir isotherm model.

Kinetic parameters were also evaluated with the First order, second order and Elovich kinetic models and found to obey Elovich rate model. The entire data has revealed that coconut coir and shell which is hitherto a serious environmental threat of the temperate region of Nigeria could be used as low cost Adsorbent/precursor for the



production of activated carbon for the remediation of heavy metal bearing industrial wastewater before final discharge into the water bodies.

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