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Adsorption Study of Utilizing Calabash (*crescentia cujete*) Seed in the Removal of Heavy Metals from Industrial Wastewater

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ABSTRACT: This work was carried out to assess the physicochemical parameters and removal of heavy metals from industrial wastewater by activated carbon prepared from calabash seed. Some physicochemical parameters of the wastewater that assessed are pH, temperature, and turbidity, BOD, COD, TS, TDS and TSS. Adsorption studies on the effects of contact time, pH and adsorbent doses on the removal of heavy metals were investigated. The pH and temperature of granite industrial wastewater were 7.5 and 32.5 respectively which are within the permissible limit of WHO (7-8.5 and 32 ^oC). The wastewater sample shows extremely high turbidity of 2.5 mg/l, biochemical oxygen demand (BOD) of 430 mg/l, chemical oxygen demand (COD) of 283 mg/l, total solid (TS) of 45 mg/l, total dissolved solid (TDS) of 655 mg/l and total suspended solid (TSS) of 965 which are above permissible limit of WHO. The maximum adsorption capacity of Zn (99%) and Fe (88%) were observed at pH 8 and 12 respectively. The pseudo-fist order and pseudo-second order kinetic models were used to fit the kinetic data of the adsorption process, and the result obtained showed that pseudo-second order kinetic model was able to fit the generated adsorption data from the heavy metals considered in this research work due to the regression coefficient R^2 of 0.997 value obtained. The study reveals that granite industrial wastewater effluent is one of the industries responsible for polluting the surrounding aquatic environment.

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Pollution by the discharge of heavy metals into the environment has become a matter of concern over the last few decades. Numerous industries such as electroplating, steel and nonferrous processes, metal finishing operations, electronic circuit production, fine-chemical and pharmaceutical production discharge a variety of toxic heavy metals into the environments (Abdus-salam and Adekola, 2005).

Several researchers have published many research works on the application of agricultural raw materials as good substrates for the removal of metal ions from aqueous solutions and wastewaters. This process attributes to the uses of waste to treat waste and become even more effective because these agricultural by–products are readily available and often pose waste disposal problems. Hence, they can be easily sourced at little or no cost because they are waste products. Also, this makes the process of remediating wastewaters with agricultural material adsorbents more economical than using conventional adsorbents like commercial activated carbon. In addition, the complicated regeneration is no need for adsorption process when using agricultural by–products for wastewater treatment (Abia and Igwe, 2005).

From several literature conducted it has reveals that no research work has reported the Physico-chemical characterization and potential of calabash (*crescentia cujete*) seed in the removal of Fe and Zn from industrial wastewater. Hence, the objective of this paper is to investigate and report the physicochemical properties of calabash seed and convert the seed to activated carbon for the removal of some heavy metals in industrial wastewater

MATERIALS AND METHODS

Collection and preparation of adsorbent: Calabash seed were obtained from Apalara in Ilorin West Local Government of Kwara State, Nigeria. The sample was sun dried for 7 days and crushed with a mortar and pestles, then sieved using 0.25nm sieve size to reduce their sizes. About 15 g of the resulting powdered sample was weighed into six different clean and pre-weighed crucibles; they were then introduced into the muffle furnace (OH85TR Gallenkamp). They were carbonized at 300 ^oC for an

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hour. The content was then removed from the muffle furnace after the set period and cooled in an open air for one hour. This process was repeated until a substantial amount of carbonized sample was obtained. Activation of the carbonaceous material produced was carried out in accordance with the description reported by Adebayo *et al*. (2015).

Wastewater Collection: The wastewater effluent from Sal/Yemic granites industrial limited located in Masaka area, Nassarawa state, Nigeria was collected in a sterile 4 L plastic container from its point of discharge to the environment. For preservation and pre-treatment, about 5 mL of 2.0 M nitric acid was added per litre of the sample. The wastewater sample was refrigerated at approximately 4 °C to avoid heavy metal precipitation and kept for further use.

Physicochemical study: The granite wastewater sample was collected and were analyzed for, pH, temperature, turbidity, Total Solids(TS), Total Dissolved Solids(TDS), Total Suspended Solids (TSS), Bio-chemical Oxygen Demand (BOD) and Chemical Oxygen Demand(COD) values. The analysis were carried in accordance to the reported by (Lokhande *et al.,* 2011)

pH: The pH of the sample was taken with the aid of hand portable pH meter by immersing its electrode into the wastewater sample and the reading was recorded.

Temperature: The temperature of the wastewater was determined at the point of wastewater sample collection with aid of mercury thermometer (0-110^{o}C) by inserting the thermometer tip into the water sample and the re4ading was recorded.

Turbidity: About 20ml of the wastewater sample was measured in a beaker, and HACH turbid meter was used to measure the turbidity and the reading was taken when it is stable.

Total Dissolved Solids: A TDS meter was used to determine the total solid, and the reading was recorded.

Total Suspended Solid: A Filter paper was dried in an oven to a constant weight and allowed to cool at room temperature. A 50 ml of wastewater sample was measured and filtered on the pre dried filter paper. The filter paper was removed gently and dried in an oven to constant weight at 10 ^{o}C. It was allowed to cool and weighed, TSS was calculated by equation 1 below:

$$TSS=\left(\frac{W_1-W_0\times 10^6}{V_S}\right) \quad (1)$$

Where W_1 is the weight of filter paper + residue and W_o is the weight of filter paper
Total solid: A total solid was determined by addition of total dissolved solids and total suspended solids.

$$TS = TDS + TSS \quad (2)$$

Biochemical Oxygen Demand (BOD): The iodometric titration method was used. A 20ml of wastewater sample was measured in reagent bottle; about 5ml of 10% $MnCl_2$ was added and 5ml of alkaline iodine solution. The bottle was corked and shaken well. A 10ml of 25% HCl was added and shaken. The mixture was titrated against 0.05M sodium thiosulphate, on appearance of pale yellow coloration, A 3 drops of starch indicator was added and titration continue to till colourless end point.

$$\text{Dissolved Oxygen}=\frac{[8000\times(V_b-V_a)\times C]}{V_S} \quad (3)$$

Where Va, Vb is the titre value for sample and blank respectively, Vs is volume of sample, therefore BOD can be calculated as:

$$BOD = DO\ 1^{st}\ day - DO\ 7^{th}\ day \quad (4)$$

Chemical Oxygen Demand (COD): The closed reflux titrimetric method was used. A 10ml of wastewater effluent was measured in a beaker, about 90ml of distilled water, 10ml of 25% H_2SO_4 and 20ml of 0.01M $KMnO_4$ was added. It was heated in water bath for 30 minutes and allowed to cool before adding 10% KI. It was titrated against 0.05M sodium thiosulphate until pale yellow coloration, few drops of starch indicator was then added and titrated to colourless.

$$COD=\frac{(A-B\times N\times 400)}{V_S} \quad (5)$$

Vs= Volume of sample

Heavy Metal Analysis: The digestion of wastewater for heavy metal analysis was done in accordance with method reported by Gin *et al.,* (2014). About 100ml of the effluent were digested using 10 mL triple acid mixture (5:1:1 - HNO_3:$HClO_4$:H_2SO_4) in a 250 mL conical flask placed in a fume cupboard and heated on a hot plate until the solution was reduced to 10 mL. Thereafter, it was allowed to cool and make up to a mark with distilled water, it was then filtered into a 50 mL standard flask labelled and made ready for further analysis. The concentrations of the heavy metals in the wastewater were determined using Atomic Absorption Spectrometer (Perkin, 210 VGP).

Sorption Experiments: Batch adsorption experiments were conducted and the effects of some selected reaction parameters on the rates of metal ions uptake from the wastewater sample using the developed activated calabash seed were investigated. The parameters considered include pH, agitation time and adsorbent dosage. These effects were carried out in accordance with the reported work of Elaigwu *et al.* (2009).

Effect of pH: A 25ml of wastewater sample were contacted with 0.2g of the adsorbent in a 100ml conical flask and the pH of the mixture was adjusted with 0.1M HCl and 0.1M NaOH and maintained to the required value of 2, 4, 6, 8, 10 and 12. The solution was agitated for 2hours, filtered and the residual metal ion concentrations were analyzed using Atomic Absorption Spectrophotometer.

Effect of contact Time: A 25 mL of the granite wastewater was measured into a conical flasks and about 0.2g of the adsorbent was weighed into a beaker and agitated for different contact time of (20, 40, 60, 80, 100 and 120 min). After each agitated time, the content of the beaker was filtered, and the equilibrium concentration of each of the metals was determined by Atomic Absorption Spectrophotometer.

Effect of Adsorbent Dose: The effect of adsorbent dosage was studied by weighing 25 mL each of the wastewater to various amounts of the adsorbent (1.0 - 3.5 g) in different conical flask and agitated on a mechanical shaker for 2hours. After completion of the reaction, conical flasks were taken out and resulting mixture were filtered and analyzed using Atomic Absorption spectrophotometer.

The % adsorbed was determined using the mass balance expression obtained from the work of Bernard *et al.* (2013).

$$\%\ \mathbf{adsorbed} = \frac{C_o - C_f}{C_o} \times 100 \qquad (6)$$

Where C_o and C_f represent the initial and final concentration of metal ions

Kinetic study profile: In kinetics profile of the activated carbon material in the adsorptive uptake of heavy metals from wastewater at different time intervals, the adsorption kinetics was studied. The pseudo-first-order and pseudo-second-order model equations are fitted to model the kinetics of heavy metals adsorption onto activated carbon. The general expression for pseudo-first-order equation model is shown in equation (7) and (8):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (7)$$

Where, q_e and q_t are the amount of metals adsorbed at equilibrium and time t, respectively. k_1 is the rate constant for the pseudo first order adsorption. The integrated rate law is given as follows

$$log(q_e - qt) = logq_e - \frac{K}{2.303} \qquad (8)$$

A plot of $log(q_e - q_t)$ against t was made and the values of k_1 and q_e were obtained from the slope and intercept, respectively.
The linear form of pseudo-second order kinetics model is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (9)$$

Where, q_e and q_t are the amount of metal ion adsorbed per unit mass of the adsorbent (in mg g^{-1}) at equilibrium and time *t,* respectively, and k_2 is the pseudo second order rate constant. A linear plot of t/q_t against t confirms the fitness of data to this model

RESULTS AND DISCUSSION

A pH is a measure of the acidity or alkalinity of water and is one of the stable measurements. A pH is a simple parameter but is extremely important, since most of the chemical reactions in aquatic environment are controlled by any change in its value. Anything either highly acidic or alkaline would kill marine life. Aquatic organisms are sensitive to pH changes and biological treatment requires pH control or monitoring. It has been reported that the toxicity of heavy metals also gets enhanced at particular pH, which is primary importance in deciding the quality of waste water effluent. Water with pH value of about 10 are exceptional and may reflect contamination by strong base such as NaOH and $Ca(OH)_2$ (Langmuir, 1997). The pH of wastewater sample obtained was 7.5 which are within the recommended standard limits of regulating bodies WHO (7.0-8.5), but slightly higher than the reported research elsewhere Lokhande *et al.,* 2011 (5.2).

Temperature is one of the most important ecological features. It controls behavioural characteristics of organisms, solubility of gases and salts in water. The basis of all life functions is complicated set of biochemical reactions that are influenced by physical factors such as temperature. Disease resistance is also linked to temperature; increase in temperature also increases the rate of microbial activity. Temperature increase may become barrier to fish movement and with this limitation is seriously affect on reproduction of species.. In the present study, the temperature of industrial effluent obtained is 32.5°C which is slightly above the permissible limits.

BOD may be defined as the rate of removal of oxygen by microorganisms in aerobic degradation of the dissolved organic matter in water over a 5-days period. It has been reported that increases in BOD can be due to heavy discharge of industrial waste water effluent, animal and crop wastes and domestic sewage. BOD values have been widely adopted as a measure of pollution effect according to WHO the maximum permitted BOD content is < 100 mg/L. The experimental data of present investigation shows that BOD value of 430 mg/L in wastewater effluent samples which were extremely higher than the permissible limit. It is important to note that low BOD content is an indicator of good quality water, while a high BOD indicates polluted water.

The Chemical Oxygen Demand (COD) determination is a measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant. It is an important, rapidly measured parameter for industrial waste water studies and control of waste treatments. COD is also one of the most common measures of pollutant organic material in water. COD is similar in function to BOD, in that both measure the amount of organic compounds in water. In the present investigation the COD values is 283 mg/L in the effluent samples It was observed that the wastewater effluent values is very much higher than 5.0 mg/L which is a maximum permissible limit according to WHO Standard.

TDS content in water is a measure for salinity. A large number of salts are found dissolved in natural waters, the common ones are carbonates, bicarbonates, chlorides, sulphates, phosphates, and nitrates of calcium, magnesium, sodium, potassium, iron, and manganese, etc. Water can be classified based on the concentration of TDS (Vilcox 1995), for desirable for drinking (up to 500 mg/L), permissible for drinking (up to 1,000 mg/L), useful for irrigation (up to 2,000 mg/L), not useful for drinking and irrigation (above 3,000 mg/L). In the present investigation, the wastewater has TDS value of 45 mg/L. Based on the above classification, it was observed that industrial wastewater effluents is within the permissible limit

The wastewater effluents is also shows high TSS and TS values of 965 mg/L and 45 mg/L respectively, which are higher than the WHO permissible limits. The table below shows the concentrations of some physicochemical parameters of granite industrial wastewater

Table 1: Physico-chemical characterization of industrial waste water analyzed

parameters	wastewater	WHO Limit
pH	7.50	7-8.5
Temperature (^{0}C)	32.5	32
Turbidity	2.5	1.5
BOD (mg/l)	430	<100
COD (mg/l)	283	5.0
TS (mg/l)	45	30
TDS (mg/l)	655	500
TSS (mg/l)	965	500
Zn (mg/l)	0.18	NI
Fe (mg/l)	0.36	NI

WHO: World Health Organization, NI: Not Indicated

Adsorption Experiment Results: Effect of pH: The initial pH of a solution is a very important factor to be considered in adsorption studies as it has been observed to play a major role in the adsorption of metal ions by various adsorbents, because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction (Badmus *et al.,* 2007).

In this study, the effect of pH on the Fe and Zn adsorption capacities of the adsorbent was conducted at various pH ranging 2-12. The role of H^+ concentration was examined from the sample at different pH. The result shows that the maximum adsorption of Fe(88%) and Zn(99%) was observed at pH 8 and 12 respectively, while the amount adsorbed increases with increases in pH. Similar trend were report in literature by Kobya *et al.,* (2005).

It was observed that as the pH of the adsorbing medium were increased from 2-12, there was a corresponding increase in deprotonation on the adsorbent surface leading to a decrease in H^+ ion on the adsorbent surface (Abdus-salam and Adekola, 2005).

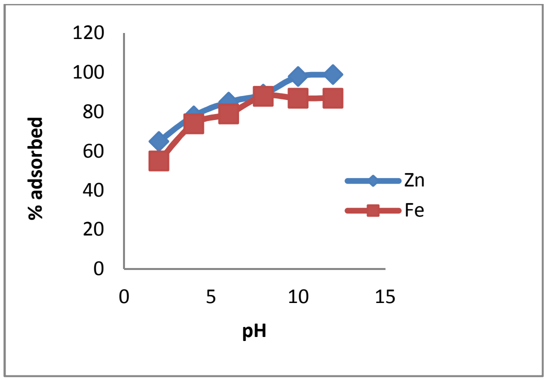

Fig 1: Effect of pH on adsorption of Zn and Fe onto activated carbon sample

Effect of contact Time: The adsorption of metal ions from aqueous solutions is controlled by the rate of reaction at which the equilibrium time is determined. The effects of contact time for the adsorption of Zn and Fe were studied between 20 and 120 minutes. The maximum amount adsorbed at different time differs for each metal ion. For Zn metal ion maximum adsorption capacity of 96% within 80 minutes of the experiment was observed; further increase in contact time had no significant effect on the adsorption capacity, The faster rate of removal of Fe 92% at 60 minutes may be due to the availability of the uncovered surface area of the adsorbents, since the adsorption kinetics depends upon the surface area of the adsorbent (Qadeer and Akhtar, 2005).

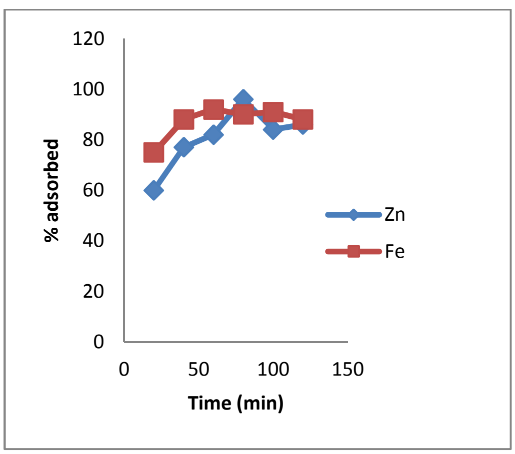

Fig 2: Effect of contact time on adsorption of Zn and Fe on to activated carbon

*Effect of Adsorbent Dose***:** In the present study, the influence of different amounts of adsorbents dose on the uptake of Zn and Fe which varies between 1.0-3.5g showed decrease in the percentage adsorbed with increase in adsorbent dosage rate. It has reported that as the number of adsorbate concentration decreases per active site, there is possibility for sorption available on the surface (Yu *et al.,* 2000). The Figure 3 shows the effect of adsorbent dose on adsorption of Zn and Fe and maximum adsorption was observed at 1.0g of adsorbent for metals, 94% and 74%. From the research work, it was observed that small amount of adsorbent gave maximum adsorption; this may be due to the high surface area and micropore volume of the activated carbon sample.

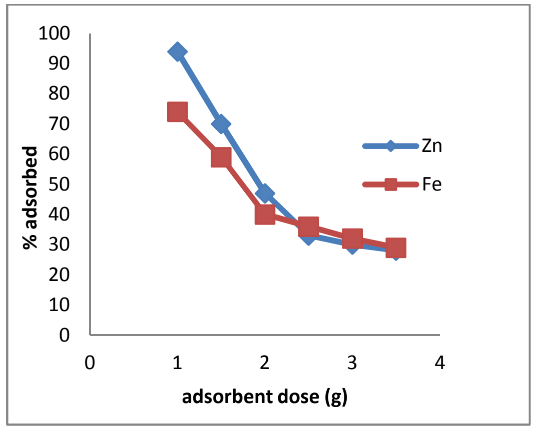

Fig 3: Effect of adsorbent dose on adsorption of Zn and Fe onto activated carbon

*Adsorption Kinetics Modeling***:** The kinetics of an adsorption is probably the most important factor in predicting the rate at which adsorption takes place in a given reaction. It is regarded as the tool used to examine the mechanism of adsorption process such as chemical reaction and mass transfer, therefore suitable methods is needed to analyze the rate data. The Lagergren's first-order kinetic model and the Ho's pseudo-second-order model are the most frequently used in the literature to predict the mechanism involved in the sorption process (Ho and McKay, 1998). In this study we used the both kinetic models to test the adsorption kinetic of both Zn and Fe onto activated carbon adsorbent.

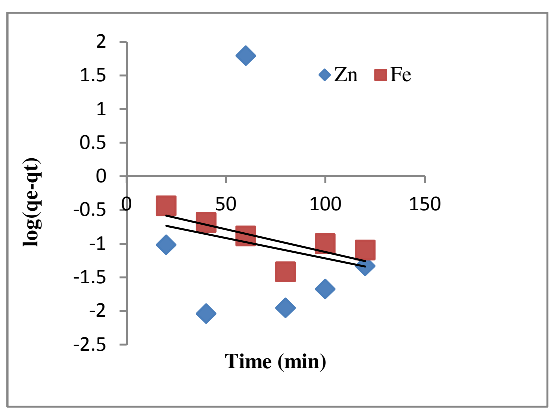

Fig 4. Pseudo-first order kinetic model for adsorption of Zn and Fe on activated carbon

Table2. Estimated coefficient of empirical kinetic models for activated carbon

Metals	Pseudo-first order			Pseudo-second order		
	K_1 (min^{-1})	qe (mg/g)	R^2	K_2(g/mgmin^{-1})	qe (mg/g)	R^2
Zn	0.008	0.378	0.006	0.555	0.121	0.951
Fe	0.006	0.703	0.528	0.086	1.846	0.997

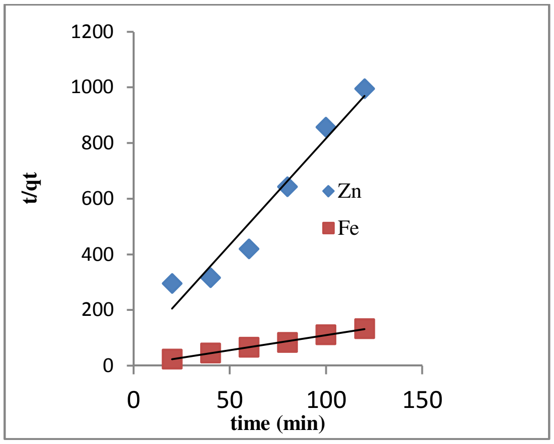

Fig 5: Pseudo-second order kinetic model for adsorption of Zn and Fe on activated carbon

Both models were examined for suitability using their correlation coefficient R^2. Comparison of the two models, it was revealed that the adsorption of the metals could best explain using the pseudo-second order. This was due to the higher correlation regression coefficient R^2 (O.997) value. It was observed from the figure 4 and 5 below that correlation regression coefficient of the sample for the second order were greater than the first order, this trend was the same as reported by Idris *et al.*, (2012).

Conclusion: Generally, all countries in the world are struggling to arrive at effective regulatory guidelines to control the discharge of industrial effluents into their various ecosystems. The present experimental data indicates high level of pollution that occurs through the discharge of granite industrial effluent in to the water body. Therefore, from the experimental results from above studies shows that activated carbon form calabash seed is an inexpensive and reliable material for the removal of toxic metals from the wastewater.

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