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Effect of Acid and Alkaline Activation of Coconut Husk based Biochar for the Removal of Cadmium (II) ion from Aqueous Solution

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ABSTRACT: In the environment, cadmium is toxic to plants, animals and micro-organisms, therefore its removal from industrial wastewater before discharging into recipient environment is necessary. The objective of this paper is to evaluate the effect of acid and alkaline activation of coconut husk based biochar for the removal of cadmium ion from aqueous solution. Data obtained reveal that coconut husk based Activated Carbon (A.C) exhibited high adsorption efficiency at a high pH of 10 with 99.8% and 99.6% of Cd (II) removal for alkaline and acid chemical activation respectively. The experimental kinetics data fit with the pseudo-second order model and the Freundlich isotherm model was found to be suitable for both type of chemical activation. Although, biochar activated with $CaCl_2$ and H_3PO_4 showed good adsorption capacity of Cd (II) metal ion in aqueous solution but the Freundlich isotherm model applied in this study with (n) values of acid and alkaline A.C to be (1.12 and 0.72) respectively, depicts that Acid A.C has shown to have a better adsorption characteristics than alkaline coconut husk based activated carbon.

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A few technologies are available with different degree of success to control water pollution. However, the disadvantages of most of these methods are high operational and maintenance costs, generation of toxic sludge and difficult procedures involved in the treatment. Comparatively, adsorption is a process considered to be better in water treatment because of convenience, easy operation and simplicity of design. Also, this process can remove or minimize different type of pollutants and thus it has a wider applicability in water pollution control. Activated carbon is undoubtedly considered as universal adsorbent for effluent treatment and is commonly used for the removal of various pollutants from water and hence has received considerable attention (Budinova *et al.*, 2008; Chen and Lin, 2001; El-Hendaway, 2005; Rao *et al.*, 2008; Satoa *et.al*, 2007). Most of these studies covered the removal of Pb^{2+}, Hg^{2+}, Ca^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Cr^{2+}, and many other such as gold (Youessef *et al.*, 2004). A large variety of non-conventional adsorbents have been examined for their ability to remove various types of pollutants from water and wastewater and have been reviewed extensively (Bhatangar and Sillanpää, 2010; Rafatullah *et al.*, 2010; Srinivasan and Viraraghavan, 2010). Most of the time, coconut husk is used as a fuel for coconut processing and as a fiber source for rope making in a relatively negligible amount. Coconut husk is the mesocarp of the coconut, which makes up 32-35% of the total fruits. Coconut husk are also relatively high in Cellulose content of about 32.5% and lignin content of about 37.9% (Rosa *et al.*, 2010). These indicate that coconut husks are potential raw material spare parts for activated carbon production. This application creates a better use of this cheap and abundant agricultural waste. The unique highly

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developed porosity and high degree of surface reactivity has made activated carbon to be widely known as a very effective adsorbent for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media or from gaseous environments (Armstrong *et al.,* 2014). With a yearly increase in population, unorganized urbanization, increasing industrialization and unspecialized utilization of natural water resources have led to the destruction of water quality in many parts of the world. In Nigeria, groundwater provides drinking water for more than one-half of the nation's population, and is the sole source of drinking water for many rural communities and some urban communities. However, due to industrial, agricultural and domestic activities, variety of chemicals can pass through the soil and potentially contaminate natural water resources and reservoirs. In recent times, various toxic compounds have been widely detected at toxic levels in drinking water in many parts of the world exposing individuals to various health risks. Due to the risk effect of elevated concentration of toxic pollutants to human health, there is an urgent need for developing cost effective and environmentally friendly processes to remove them from drinking water, sea water and rivers in other to safeguard the health of affected citizens. Therefore, the objective of this paper is to evaluate the effect of acid and alkaline activation of coconut husk based biochar for the removal of cadmium metal ion from aqueous solution.

MATERIALS AND METHODS

Coconut husk was obtained from fruit garden market in Port-Harcourt, Rivers State. Chemicals used are Calcium Chloride ($CaCl_2$), Phosphoric Acid (H_3PO_4), Hydrochloric acid (HCL) and Sodium Chloride (NaOH), all in analytical grade.

Carbonization and Activation of Coconut Husk: Coconut husk was cut, dried and ground before carbonization at 400^0C for 2 hours in a furnace. Activation of carbonized coconut husk was done using $CaCl_2$ solution (1:3) and 6M H_3PO_4 to achieve Alkaline and Acid activated carbon respectively. Biochar was soaked with the activation liquid and allowed to stay tightly covered for 24hrs. Afterwards, mixture was filtered with distilled water until neutral pH was achieved. Activation of biochar continued with oven drying of activated carbon at 200^0C for 2hrs.

Cadmium Metal Ion Absorption: The batch absorption was done in three different parameters; Adsorbent dosages, shaking time and pH level. The optimal pH of the solution for adsorption of cadmium metal ion was determined by introducing 0.5g of activated carbon into a conical flask containing 25ml of aqueous solution with a known concentration of metal ion, at a temperature of (23^0C ±0.1). After 60mins of contact time, the filtrate was collected drop after drop. The final concentration of metal ion in solution was ascertained using Atomic Absorption Spectroscopy (AAS) and the removal percentage of cadmium metal ion from the aqueous solution was calculated using equation (1). pH adjustment was done using 0.1M HCL and 0.1M NaOH. The same procedure was repeated while varying the adsorbent dosage and contact time leaving all other variables constant.

Table 1: Controllable Factors on adsorption of cadmium (II) ion

pH	Temperature (^{0}C)	Adsorbent Dosage (g)	Solution Volume (ml)	Contact Time (min)	Co (mg/L)
2	22	0.5	25	60	6704
4	22	0.5	25	60	6704
6	22	0.5	25	60	6704
8	22	0.5	25	60	6704
10	22	0.5	25	60	6704
6	22	0.1	25	60	6704
6	22	0.6	25	60	6704
6	22	1.1	25	60	6704
6	22	1.6	25	60	6704
6	22	2.1	25	60	6704
6	22	0.5	25	10	6704
6	22	0.5	25	20	6704
6	22	0.5	25	30	6704
6	22	0.5	25	40	6704
6	22	0.5	25	50	6704

The amount of adsorbate (Cd^{2+}) removed at equilibrium by chemical activated adsorbent was calculated using equation (2). The amount of solutes removed at a given time by the adsorbent was also determined using equation (3).

$$R(\%) = \frac{C_0 - C_1}{C_0} \times_{100} \quad \text{……… (1)}$$

$$q_e = \frac{C_i - Ce}{w} \times \text{V} \quad \text{………….. (2)}$$

$$q_t = \frac{C_i - C_e}{w} \times V \quad \ldots\ldots\ldots\ldots\ldots (3)$$

Where; Co and Ci (mg/L) is the initial metal ion concentration in the solution before adsorption, Ce and Ct is equilibrium concentration of metal ion after adsorption. V (litre) is the volume of sample (25ml) and W (gram) is the weight of adsorbent (0.5g).

RESULTS AND DICUSSION

Morphology of Biochar from Coconut Husk: Scanning Electron Microscopy (SEM) images captured from the surface of biochar and activated coconut husk based biochar used in this research is shown in figure (1). SEM showed several changes on the surface of the composite after chemical modification. SEM images of activated biochar showed porous surfaces for both acid and alkaline coconut husk based biochar compared to unmodified coconut husk based biochar.

Influence of pH on Cd^{2+} Adsorption: The process of metal ion adsorption by coconut husk activated carbon is significantly affected by the solution pH. The effect of pH on the adsorption of Cd^{2+} was investigated in the range of 2-10, using 0.5g of activated carbon (acid and alkaline) 25ml solution of 6704mg/L of Cd^{2+} ions, with agitation for 50mins at a speed of 400rpm at ambient temperature (23^0C $\pm 0.1^0$C).

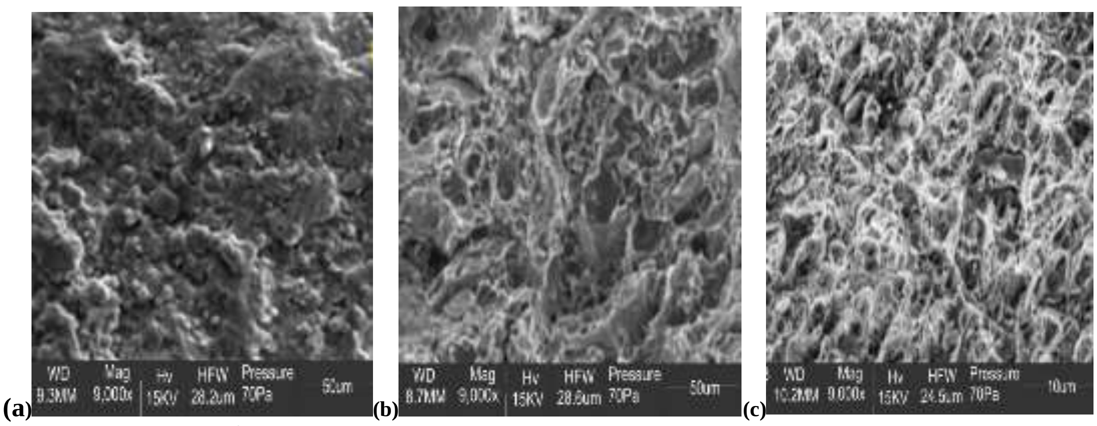

Fig 1: SEM images of; (a) Coconut Husk Based Biochar (b) Alkaline Activated Biochar (c) Acid Activated Biochar.

The results are shown in figure 2, it was observed that at low pH values (pH < 6), the metal tend to be minimally retained by both the acid and alkaline activated carbon. The activated carbon preferably absorbs hydrogen ion (H^+) from solution than the heavy metal ion, and therefore, in more acidic condition, more H^+ ions are absorbed from solutions. However, with increasing pH, the competition for hydrogen ion is reduced and the positively charged Cd^{2+} can be adsorbed at the negatively charged sites on the adsorbent. The removal optimum was at pH value of 10 for both acid and alkaline activated carbon with alkaline chemical activated carbon having the highest removal percentage.

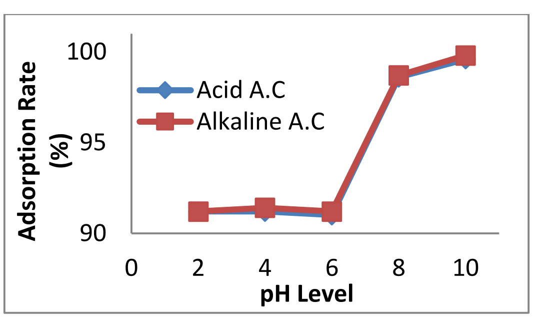

Fig.2: Effect of pH of Aqueous Solution on the Adsorption Rate of Cd^{2+} in both Acid and Alkaline Activated Carbon.

Effect of Adsorbent Dosage: The effects of different adsorbent dosages on metal ion removal for both acid and alkaline activated carbonized coconut husk are illustrated in figure (3). The adsorbent dosage varied from 0.1 – 2.1 g/25ml. the initial Cd^{2+} concentration, stirring speed, contact time, initial pH and temperature were 6704 mg/L, 400rpm, 60mins, 6 and (23℃ ± 0.1℃) respectively. It is observed from figure (3) that the removal efficiency of adsorbents was dependent on increase in adsorbent dosage, the higher the dosage, and the greater the removal percentage.

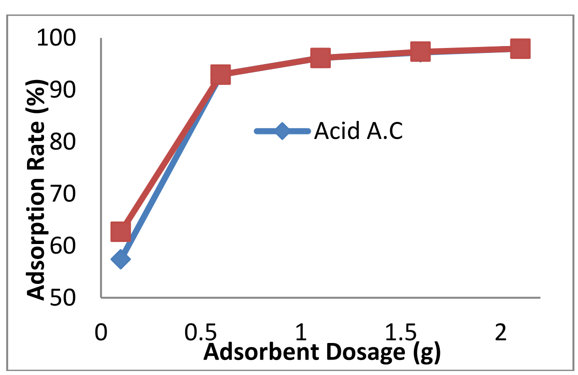

Fig.3: Graph Showing the Effect of Adsorbent Dose on the Removal Percentage of Cd^{2+} by Acid and Alkaline Activated Carbon.

Effect of Shaking Time: The influence of shaking time on removal percentage of metal ions was observed using a constant concentration of Cd^{2+} at ambient temperature (23℃ ± 0.1℃) to ascertain the optimum contact time for metal ion removal by acid and alkaline activated carbon. The applied time intervals were 10, 20, 30, 40, and 50 (mins). Figure (4) shows the findings.

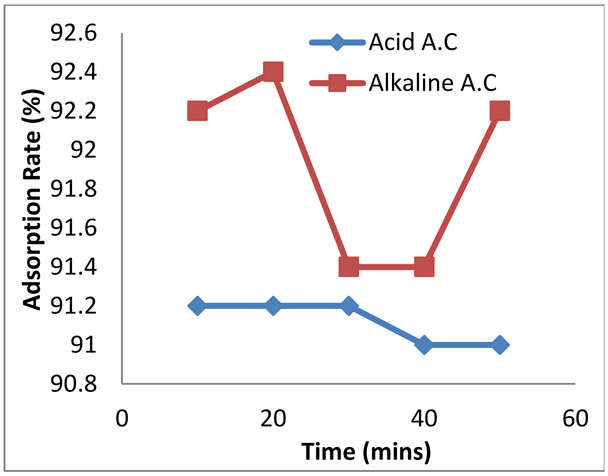

Fig.4: Graph Showing Cd^{2+} removal by Acid and Alkaline Activated Biochar at Different Time intervals.

As shown, with reduced contact time, the percentage removal of Cd^{2+} by Acid activated coconut husk remained constant until it got to 40mins were it began to drop completely. Furthermore, alkaline activated carbon, attained a very high removal percentage from 10-20mins, dropped at 30-40mins and later increased at 50mins.

Adsorption Kinetic Studies: The adsorption kinetic studies of Cd^{2+} ion by coconut husks were done using the pseudo-second order model. The model was fitted to the experimental data using regression techniques, and the model's coefficients were determined also. The pseudo-second order kinetics is described using equation (4).

$$\frac{t}{qt} = \frac{1}{k2{q_e}^2} + \frac{1}{qe} \quad \text{……….. (4)}$$

Where qt and qe are the amount of heavy metal ions absorbed (mg/g) at time t (min) and equilibrium, respectively and K2 is the second order reaction rate constant (g/mg min). A plot of t/qt values versus t resulted in a linear behavior for the application of pseudo-second order kinetic model. The value of R square is 1 and this suggests that model is suitable for the experiment for both type of chemical activation.

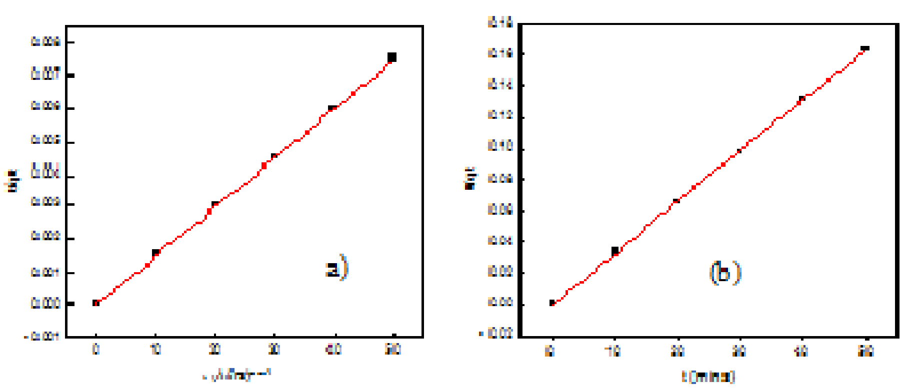

Fig 5: **a)** pseudo-second order plot for the adsorption of Cd^{2+} by Alkaline Activated Carbon **b)** pseudo-second order plot for the adsorption of Cd^{2+} by Acid Activated Carbon

Table 2: Coefficients of pseudo-second order kinetics describing the adsorption of Cd^{2+} by both Acid and Alkaline Activated Carbon from Coconut Husks

Pseudo-Second Order Kinetics					
Alkaline Activated Carbon			**Acid Activated Carbon**		
R^2	K2	qe	R^2	K2	Qe
1.00E+00	-3.40E+15	6.68E+03	1	-1.20E-01	304.9

Adsorption Isotherm Model: In this research, Freundlich isotherm model was applied to demonstrate the adsorption equilibrium data. The Freundlich isotherm is deduced as;

$$\text{Log}\, qe = \text{Log}\, k_f + \frac{1}{n}\text{Log}\, Ce \quad \text{……… (5)}$$

Where qe is the amount of heavy metal ions absorbed (mg/g), Kf is the Freundlich constant, n is the heterogeneity factor and Ce is equilibrium concentration of metal ion after adsorption. The n value of Freundlich equation indicates the favorability of adsorption. Values of n in the range of 1-10, and those less than 1, represents good and poor adsorption characteristics respectively (Meroufel *et. al*, 2013). Graph of Log Ce versus Log qe gave a linear relation R^2 (1 and 0.999) for alkaline and acid activated carbon respectively. This implies that the model is appropriate to explain the adsorption of Cd (II) by both type of chemical activated biochar. However, the n value for alkaline A.C and acid A.C is 0.715 and 1.12 respectively which shows that acid activated carbon give a better adsorption characteristics than alkaline activated biochar.

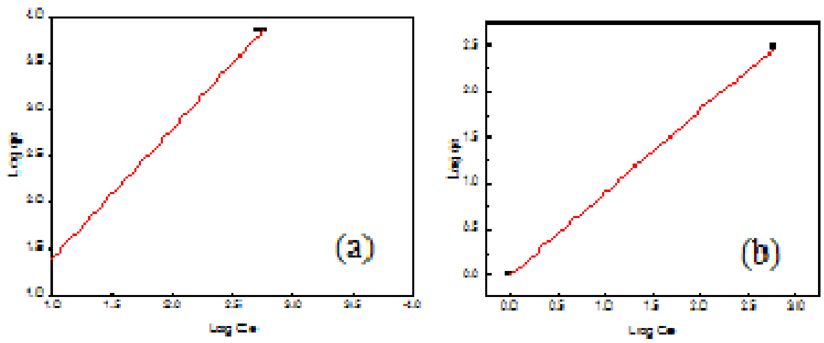

Fig 6: (a) Freundlich Isotherm plot for the adsorption of Cd^{2+} by Alkaline Activated Carbon **(b)** Freundlich Isotherm plot for the adsorption of Cd^{2+} by Acid Activated Carbon

Table 3: Coefficients of Freundlich Isotherm describing the adsorption of Cd^{2+} by both Acid and Alkaline Activated Carbon from Coconut Husks

Freundlich Isotherm model							
Alkaline Activated Carbon				**Acid Activated Carbon**			
R^2	Kf	1/n	N	R^2	Kf	1/n	N
1	1.003	1.3985	0.7151	0.999	1	0.896	1.116

Conclusion: This research showed that chemically modified biochar prepared from coconut husks is effective for the removal of Cd (II) metal ions from waste water. The process of adsorption was found to be highly dependent on pH of aqueous solution and adsorbent dosage for both types of chemical activated biochar. However, the chemical activation of biochar using $CaCl_2$ and H_3PO_4 showed no significant difference in adsorption capacity but from the Freundlich isotherm model applied in this study, which depicts important role in showing the interaction between adsorbate, adsorbent and the optimum adsorption capacity of adsorbent, we can deduce from the n values of acid and alkaline activated carbon that the coconut husk based biochar with acid chemical activation, has shown to have a better adsorption characteristics.

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