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Der Chemica Sinica, 2015, 6(3): 76-82



Kinetic and equilibrium studies on the selective removal of heavy metal by Neem seed and husks using column adsorption studies

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ABSTRACT

The activated carbon were produced from neem (Azadirachta Indica) husk and seed and activated with $ZnCl_2$ and H_3PO_4 . The prepared adsorbents were used to adsorb heavy metals (Cd, Cr, Ni, Zn and Pb) in a multi-component system. The extent of adsorption of the metals were in this order; Cr (82%), Pb (70%), Ni (61%), Zn (59%) and Cd (36%). The kinetics study was studied using Pseudo-second-order rate model and Weber-Morris Intraparticle Diffusion Model (WMIDM) while the adsorption isotherms were studied using Langmuir and Freundlich Adsorption Isotherm. The adsorption isotherms best fit the Langmuir Adsorption Isotherm relative to the Freundlich Isotherm.

Keywords: Adsorption, activation, neem husk and seed

INTRODUCTION

It has been reported that the global demand of activated carbon was above 500,300t as at 2003, and it is expected to rise annually by 7% (Maroto-Valer et al., 2001). Due to the increasing market demand for activated carbon, it is imperative to investigate alternative cheap and readily available precursors. Neem (*Azadirachta Indica*) plant is wide spread in the tropical countries while in Nigeria it is common in the northern part of the country [20]. In the past, it has been used for pest harvest storage, neem bio pesticide for pest control, neem cake as fertilizer, neem oil for skin infection, dandruff, eczema, organo-mineral compound as fertilizer for all crops, neem-coated with urea (lasts longer), bio- Nimbecidine (Grains insects' control), bio-Cure (fungicide), bio-ant termites, alsoft neem oil (Braid spray), repelling gel (Mosquito repellant), neem active toothpaste, activated carbon and neem soap [2]. Other agricultural wastes used as activated carbons include; silk cotton ball, coconut tree sawdust, maize cob and banana pith, coconut shell [10] coconut husk and goat hair [4], bamboo dust, groundnut shell, rice husk and straw [16], Hazelnut shell [6], pecan shells [5], Neem husk [2]. The conversion of this agricultural waste into activated carbons which can be used as adsorbent in waste water purification or the treatment of industrial and municipal effluents provide a potential and cheap alternative to existing commercial carbons.

MATERIALS AND METHODS

2.1 Materials

Neem husk and cake were collected from the National Research Institute for Chemical Technology (NARICT) Basawa, Zaria, and sundried for 3 days while the waste water was collected from Abuja Teaching Hospital, Gwagwalada.

2.2 Methods

The following physico-chemical parameters were investigated before and after sorption: Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Turbidity Test, Conductivity, Total Dissolved Solid (TDS), Determination of Total Solids (TS) and Determination of Metal Ions (Fe, Cr, Co, Ni and Pb).

2.3 Adsorption Studies

The wastewater (150ml) was mixed with each activated carbon from Neem husk and seed (1, 5, 10, 15, 20 and 25g) in 250ml Erlenmeyer flasks. The wastewater was then allowed to pass through the adsorbent bed. The filtrate was analyzed to determine the amount of the wastewater component that has been adsorbed. The process was repeated varying Activated Carbon type, time of adsorption and sorbent dosage.

RESULTS AND DISCUSSION

3.1 Waste water Characterization

	After treatment with					
Parameters	RWW	NSZ	NSH	NHZ	NHH	DWS
pH	6.4	5.78	5.74	5.27	5.07	7
Conductivity (µs/cm)	77	53.4	17	19.47	28.9	-
TDS (g/L)	40.36	30.9	8.78	10.22	15.75	500
Turbidity (NTU)	56	0	5	5	0	5
COD (mg/L)	280	215	190	190	210	255a
BOD (mg/L)	15	7	11	11	7	4b
DO (mg/L)	39	30	38	39	38	-
Cadmium, Cd (mg/L)	0.122	0.102	0.098	0.078	0.094	0.003
Chromium, Cr (mg/L)	0.733	0.312	0.526	0.133	0.386	0.05
Zinc, Zn (mg/L)	4.239	7.021	1.736	7.345	2.404	3
Nickel, Ni (mg/L)	3.801	1.468	1.907	1.746	2.215	0.02
Lead, Pb (mg/L)	1.97	0.59	1.59	1.59	1.34	0.1

Table 1 Properties of Hospital wastewater before and after treatment with adsorbents

RWW represents Raw Wastewater; *NSZ* and *NSH* values are the values of the parameters in wastewater after treating with Neem Seed carbon activated with $ZnCl_2$ and H_3PO_4 respectively; *NHZ* and *NHH* are the values of the parameters treated of the tested parameters in wastewater after treating with Neem Seed carbon activated with $ZnCl_2$ and H_3PO_4 respectively; *NHZ* and *NHH* are the values of the parameters treated of the tested parameters in wastewater after treating with Neem Seed carbon activated with $ZnCl_2$ and H_3PO_4 respectively; *COD* represents the Chemical Oxygen demand; *DO* is the dissolved Oxygen and *BOD* is the Biological Oxygen Demand: *DWS* represent Drinking Water standard as listed in NIS 2007; [7] and [19].

3.2 Adsorption Studies

The waste water was treated with the different adsorbents from neen [Neem Seed activated with $ZnCl_2$ (NSZ), Neem Seed activated with H_3PO_4 (NSH), Neem Husk activated with $ZnCl_2$ (NHS) and Neem Husk activated with H_3PO_4 (NHH)]. The above table shows the results of the raw waste water and the treated waste water. The order of effectiveness of the four different neem adsorbents on Cr are in this order; NHZ (82%), NSZ (52%), NHH (47%) and NSH (27%). For Pb, NSZ (70%) was the most efficient followed by NHH (32%), while NSH and NHZ both had 19%. The pattern of efficiency of the adsorbents on Ni is in this order; NSZ (61%), NHZ (54%), NSH (50%) and NHH (42%). Zn was adsorbed most by NSH (59%) followed by NHH (43%) while NSZ and NHZ rather added to the concentration of Zn by 66% and 73% respectively. Cd was the least adsorbed among the metals studies with NHZ as the most effective adsorbent (36%), followed by NHH (23%), then NSH (20%) and then NSZ (16%). In summary Cr had the highest adsorption of 82% followed by Pb (70%) then Ni (61%), Zn (59%) and lastly Cd (36%).

3.3 Kinetic Studies on wastewater treatment

3.3.1 Effect of contact time

The effects of contact time on the values of the treated parameters are shown in Figures 1 to 5. The effect of contact time was investigated by varying the time (10, 15, 20, 25 and 30 minutes) at which the waste water samples stayed in the columns with the activated carbon materials at a constant flow rate of 6 ml/min. The results were further analysed with the Pseudo-Second-order rate kinetic model and the Weber and Morris Intraparticle diffusion model. All samples showed a great increase in the initial 10 minutes, possibly, at the beginning, the solute molecules were adsorbed by the exterior surface of adsorbent particles, so the adsorption rate was faster due to availability of viable sites but as time of adsorption increases to the 20 minutes mark, the increase was mild despite the increase in time. This is indicative of attainment of equilibrium. When the adsorption of the exterior surface of the particle. This phenomenon allows relatively long contact time. The values for Ni²⁺ at 20 minutes show a strange deviation from the pattern. There is an increase in Nickel content at 20 minutes. The presence of other ions in the solution affects the adsorption of a particular ion of interest compete with each other for the available adsorbent sites. Those having the greater ionic potential (ratio of charge to ionic radius) or the most electronegative ions would be removed first and if the sites were still under saturated, then those having lower ionic potential or lower electro negativity would

be removed in the sequence [23]. To further explain the mechanism of adsorption of these metals, the data has been treated with the Pseudo-second-order rate and Weber and Morris Intraparticle Diffusion kinetic models.





Figure 2 Effect of contact time on Cd ion concentration of treated wastewater



Figure 3 Effect of contact time on Chromium ion level in treated wastewater



Figure 4 Effect of contact time on Nickel ion level in treated wastewater



Figure 5 Effect of contact time on Lead ion concentration of treated wastewater

3.4 The Pseudo-second-order rate kinetic model

The data for the time dependence on the removal of some of the tested parameters by the activated carbon samples have been subjected to the linearized Pseudo-second-order rate model equation of [13]. Based on equilibrium adsorption, the linearized pseudo-second-order kinetic equation is expressed as

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$$

Where q_t (mg/g) is the amount of adsorbate retained at time, t (min). Plots of t/q_t versus t for the activated carbon samples plotted and the value of the adsorption capacity of the activated carbons q_e , the pseudo-second-order rate constant k_2 , (g/mg min) the initial adsorption rate constant h (mg/g min), and the coefficient of determination \mathbb{R}^2 were evaluated from the plot. The constants k_2 and h were calculated respectively from the intercept and slope of the linear plots obtained. The straight lines in the plots prove a good agreement of experimental data with the secondorder kinetic model. According to [13], if the plot is linear, then the adsorption process may be described as chemisorption. The results shows that the kinetics of pollutant adsorption onto activated carbons follow this model with correlation coefficients greater than 0.75. These results imply that chemisorption mechanism plays an important role for the adsorption of the pollutants onto activated carbons.

The Intraparticle Diffusion Model

The possibility that the diffusion mechanism might be the rate limiting stage in regard to the entire process was evaluated by the linear dependence on the Weber-Morris Intraparticle Diffusion Model (WMIDM) [25]. Intraparticle diffusion is a transport process involving movement of species from the bulk of the solution to the solid phase [24]. The intraparticle diffusion model has therefore been integrated to explain the diffusion and describe the adsorption process occurring within the internal pores of the adsorbent. The kinetic data were fitted into the linear equation of the diffusion model developed by [25]:

 $q_e = k_{id}t + C_i$

A plot of the amount of adsorbate sorbed, q_t (g/g) and the square root of the time t, gives the rate constant k_{id} (gg⁻¹ min^{-1/2}) which is the intraparticle diffusion rate coefficient as the slope of the plot and C_i (g/g) which is the intraparticle diffusion coefficient as the intercept of the line accounting the bonding effect between the activating agent and the carbon. Larger k_{id} values illustrate better adsorption which is related to improve bonding between adsorbate and adsorbent particles and may simply be due to the fact that higher adsorbate concentration adds to a greater driving force for diffusion of adsorbate molecules into the pores [22]. K_{id}, R² values have also been calculated. According to [27], the adsorption mechanism assumes intraparticle diffusion if the following conditions are met: (i) High R² values to ascertain applicability; (ii) Straight line which passes through the origin for the plot area q_t vs. $t^{1/2}$; (iii) Intercept C_i < 0. A validity test which deviates from (ii) and (iii) above shows that the mode of transport is affected by more than one process which means that two or more stages occur. The results obtained indicate that none of the straight lines passed through the origin i.e. $C_i > 0$ for all cases, suggesting that intra-particle diffusion was not the only rate-controlling step. According to [7], when the plots do not pass through the origin, it is indicative of some degree of boundary layer control and this further show that the intra-particle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously. The packing density of the activated carbon can be responsible for these phenomena owing to the fact that the effect of initial contact time illustrated that the contact with the surface directly affected the sorption procedure. Probably, the initial stages were controlled by external mass transfer or surface diffusion, followed by chemical reaction or a constant-rate stage, and diffusion causing gradual decrease of the process rate. It is therefore unlikely that a number of ion/molecules diffuse into the pore before being sorbed.

3.5 Effect of initial wastewater on mineral/chemical parameters

The effects of initial concentration on the values of the heavy metals were studies. It was observed that the zinc ion concentration increased after treating with ZnCl₂ activated carbon samples, NSZ and NHZ. These increases stem from the enrichment of the treated water with zinc from the surface of the adsorbent. A contrary effect is shown in the samples NSH and NHH which shows a decrease in the first 10ml and then no significant change, as a result of equilibrium. Except for the NHH values of Nickel concentration, this shows a relatively high value. NSH, NHZ and NHH follow the regular pattern of decrease and increase but at different capacities. This pattern indicates the formation of monolayer coverage at the outer interface of the adsorbents at the early stage [1]. In a multicomponent system such as the wastewater, the presences of some ions in the solution affect the adsorption of other rival ion of interest and compete with each other for the available adsorbent sites. Those having the greater ionic potential (ratio of charge to ionic radius) or the most electronegative ones would be removed first and if the sites were still under saturated, then those having lower ionic potential or lower electronegativity would be removed in the sequence [23]. To further explain the manner of adsorption of these metals, the data has been treated with the Langmuir and the Freundlich adsorption isotherm.

3.6 The Langmuir sorption Isotherm

To correlate the adsorption equilibrium data, Langmuir and Freundlich models are employed. Langmuir model has the form of

$$1/q_e = 1/C_e q_m b + 1/q_m$$

Where q_e is the amount of adsorptate (g) accumulated per gram of activated carbon material used; C_e is the residual amount of adsorbate in water at equilibrium, q_{m} , a constant related to adsorption capacity (mg/g), is the maximum specific uptake for a monolayer coverage corresponding to the site saturation and *b*, the Langmuir constant related to energy of adsorption, is the ratio of adsorption and desorption rates. The adsorption equilibrium data for COD, and the chemical parameters on the activated carbons samples were analysed in terms of the Langmuir isotherm model. The constant *b* expresses the affinity between the adsorbent and adsorbate. The parameters q_m and *b* were obtained from the slopes and intercepts respectively. The essential characteristic of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which is defined as:

$$RL = 1/(1 + b Co)$$

where b is the Langmuir constant and C_0 is the initial concentration of the metal ions. The R_L value indicates the shape of the isotherm. R_L values between 0 and 1 indicate favourable absorption. Also R_L values equal to 0 indicate irreversible absorption, R_L = 1 is linear and R_L > 1 is unfavorable. Most of the R_L values listed in Table 2 were between 0 and 1.

3.7Freundlich adsorption isotherm

The Freundlich isotherm has been chosen to estimate the adsorption intensity of the adsorbent towards the adsorbate. Apart from a homogeneous surface, the Freundlich equation is also suitable for a highly heterogeneous surface and

an adsorption isotherm lacking a plateau, indicating a multi-layer adsorption. The linearized form of Freundlich adsorption isotherm [9] was used to evaluate the sorption data and is represented as:

 $Inq = In_{KF} + 1/n In C_{eq}$

Where C_{eq} is the equilibrium concentration (mg/l), q is the amount adsorbed (mg/g) and K_F and n are constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity respectively. The magnitude of K_F and n shows easy separation of metal ion from wastewater and high adsorption capacity and determine the steepness and curvature of the isotherm. The values of K_F and n were calculated from the intercepts and slopes of the Freundlich plots respectively. According to [15], n values between 1 and 10 represent beneficial adsorption. According to [14] if the values of n are found to be negative it indicates unfavourable adsorption. The values of n for all parameters were found to be less than 1 and negative. The higher the K_F value the greater the adsorption intensity. The R^2 value of the Freundlich isotherm was higher than those in the corresponding Langmuir Isotherm, showing that the pattern of adsorption is heterogeneous.

CONCLUSION

The study has shown that the neem carbon activated with $ZnCl_2$ and H_3PO_4 were very effective in treating multicomponent system from hospital waste. The adsorbents efficiently adsorbed 82% of the chromium in the waste water, followed by70% lead, 61% of Nickel, then 59% of zinc and lastly 36% of cadmium. When subjected to Pseudo-second-order rate model equation of Ho and McKay, (1998), it was observed the kinetics of pollutant adsorption onto activated carbons follow this model with a correlation coefficients greater than 0.75. These results imply that chemisorption mechanism plays an important role for the adsorption of the pollutants onto activated carbons. The Weber-Morris Intraparticle Diffusion Model (WMIDM) [25] was used to ascertain the possibility weather the diffusion mechanism might be the rate limiting stage in regard to the entire process but the result shows that the intra-particle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously. The pattern of the adsorption of these metals was studied by subjecting the results with the Langmuir and the Freundlich adsorption isotherm. The result shows that adsorption pattern fit best to the Langmuir compared to the Freundlich adsorption isotherm.

Acknowledgement

The author gives thanks to Almighty God for the grace and ability to conduct this study. Also, extends appreciation to Prof. C.E. Gimba, Prof. Agbaji and Dr Abeche for their helpful comments on the manuscript. I want to specially thank God for my parents, Dr and Mrs. Donatus Alau, for their continuous support, encouragement and parental love, care and concern to see me successful. I will not forget my wife and children, brothers and sisters, friends and colleagues and all the authors and references used for this study.

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