Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **1(6),** 53-58, Sept. **(2011)** *Res.J.Chem.Sci.*

Preparation of Activated Carbon from Nipa Palm Nut: Influence of Preparation Conditions

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Available online at: www.isca.in
(Received 23rd July 2011, revised 1st August 2011, accepted 17th August 2011)

Abstract

In this study, nipa palm nut (NPN) was used to prepare activated carbon for the removal of lead (11) from aqueous solution. Chemical activation method using phosphoric acid was employed. Full factorial design of experiment was used to correlate the preparation variables (activation temperature, activation time and acid impregnation ratio) to the lead uptake from aqueous solution. The optimum conditions for preparing activated carbon from NPN for Pb^{2+} adsorption were as follows: activation temperature of 500^0C, activation time of 1hr and acid impregnation ratio of 1:2 (acid/precursor, wt basis) which resulted in 99.88% uptake of Pb^{2+} and 30.20% of activated carbon yield. The experimental results obtained agreed satisfactorily with the model predictions. The equilibrium data for adsorption of Pb^{2+} on the optimum activated carbon were well described by the Langmuir isotherm model. The results of adsorption studies showed that activated carbon produced from NPN is a very efficient adsorbent for the removal of Pb^{2+} from aqueous solutions.

Keywords: Preparation, adsorption, lead, nipa palm nut.

Introduction

Activated carbons are becoming more and more interesting on account of their excellent properties as adsorbents, which make it possible to use them in purification and pollutant removal from both liquid and gaseous media[1]. Their adsorptive properties are due to their surface area, a micro porous structure, and a high degree of surface reactivity. Activated carbons are usually obtained from materials with high carbon content and possess a great adsorption capacity, which is mainly determined by their porous structure[2]. The inherent nature of the precursor or starting material, as well as the method and conditions employed for carbon synthesis, strongly affects the final pore size distribution and the adsorption properties of the activated carbons[3]. In recent years, special emphasis on the preparation of activated carbons from several agricultural by products has been given due to the growing interest in low cost activated carbons from renewable biomass, especially for applications concerning treatment of drinking water and wastewater[4]. The selection of solid wastes as precursor for activated carbon depends on the potential for obtaining high quality activated carbon, presence of minimum inorganic, volume and cost of raw materials and storage life of raw materials[5].

There are two methods of preparing activated carbons: physical and chemical activation. The advantage of chemical activation over physical activation is that it is performed in one step and at relatively low temperatures. The most important and commonly used activating agents are phosphoric acid, zinc chloride and alkaline metal compounds, such as KOH[6, 7]. Phosphorous acid activation only involves a single heat treatment step and activation is achieved at lower temperatures. Higher yields are obtained and most of the phosphoric acid can be recovered after the process is completed. In addition, the use of chemical reagents allows another degree of freedom in the choice of process conditions[8]. The present study is directed towards optimizing the conditions for the preparation of activated carbon from nipa palm nut for the removal of Pb^{2+} from aqueous solution

Material and Methods

Preparation of activated carbon: 100g of each raw material was impregnated with concentrated ortho-phosphoric acid at different ratios of acid to raw material (1:1, 1:1 and 1:2) on weight basis as shown in Table-2. The impregnated samples were dried in a Memmert oven at 120^0C for 24hours. One step activation of the samples was performed in KGYV Budapest muffle furnace. The samples (20g each) were carbonized for 1hr, $1^1/_2$hrs and 2hrs at 500^0C, 650^0C and 800^0C according to design of experiment in Table-2. After cooling to the ambient temperature, the samples were weighed in order to determine the yield of activated carbon from the materials. The samples were washed with de-ionized water several times until pH 6-7, filtered with Whatman No.1 filter paper and then dried in the oven at 110^0C for 8 hours. The dried samples were pulverized, sieved and then stored in air tight bottles ready for use. Full factorial experimental design for the production of activated carbon and factor levels of the independent variables for the production of activated carbon are shown in table -1 and table- 2 respectively.

Table -1
Full factorial experimental design for the production of activated carbon

Run	Coded values	Natural values		
		Temp of activation ^{0}C	Activation time (hour)	Impregnation ratio Acid: raw material
1	+ + +	800	2	2
2	- + +	500	2	2
3	+ - +	800	1	2
4	- - +	500	1	2
5	+ + -	800	2	1
6	- + -	500	2	1
7	+ - -	800	1	1
8	- - -	500	1	1

Table -2
Factor levels of the independent variables for the production of activated carbon

Independent variables	Low level (-1)	Medium level (0)	High level (+1)
Temperature, ^{0}C	500	650	800
Carbonization time, min	60	90	120
Acid concentration/raw material ratio (wt)	1	1.5	2.0

Characterization of activated carbon: Determination of pH of activated carbon: The pH of the carbon was determined using standard test of ASTM D 3838-80[9]. Determination of moisture content: Moisture content of activated carbon and raw materials was determined using ASTM D 2867-91[10]. Determination of bulk density of activated carbon: The bulk density of the activated carbon was determined according to the tamping procedure by Ahmedna et al[11]. Determination of volatile content: 1.0g of sample was weighed and placed in a partially closed crucible of known weight. It was heated in a muffle furnace at 900^{0}C for 10mins. Determination of percentage fixed carbon: The percentage fixed carbon is given by:

100 – (Moisture content + ash content + volatile matter) %. Determination of iodine number of activated carbon: The iodine number was determined based on ASTM D 4607-86[12] by using the sodium thiosulphate volumetric method. Determination of surface area: The specific surface area of the activated carbon was estimated using Sear's method[13, 14]

Adsorbate preparation and adsorption study: The reagents used were lead nitrate salt $Pb(N0_3)_2$, and de-ionized water. The reagents were of high grade. The sample $Pb(N0_{32})$ was dried in an oven for 2hrs at 105^{0}C to remove moisture. 1.6g of $Pb(N0_3)_2$ was dissolved in 1000ml of de-ionized water to get the stock solution of 1000g/l. A known weight of activated carbon was added to 100ml of the 100mg/l of adsorbate in a conical flask and placed on a magnetic stirrer. The stirring was done at 30^{0}C for 3 hours. After adsorption is complete, the solution was filtered using Whatman no.1 filter paper. The residual Pb^{2+} concentrations of the effluent were determined spectrophotomically using atomic adsorption spectrophotometer at 217.0nm wavelength. The percentage adsorbed was calculated from equation 1.

$$\% \ Adsorbed = [(C_o - C_e)/C_o]\ x\ 100 \quad \ldots.. 1$$

Where, C_o and C_e are the metal concentrations (mg/l) at initial and any time t, respectively, and V the volume of the solution (l). The effects of particle size, adsorbent dosage and pH were studied.

Results and Discussion

Yield of activated carbon from NPN: The yield of activated carbons was calculated from sample weight after activation to its initial weight. Figure-1 shows the percentage yield of activated carbons prepared at different conditions of temperature, time, and acid/precursor ratio. It is seen that yield decreased with increase in temperature and time. Similar results were obtained by[15]. Increasing the weight of phosphoric acid decreased the yield. A similar trend was reported by Wan Nik et al[16]. The low yield at high temperature was essentially the devolatization of the raw material upon heating[17]. Maximum yield of 34% was recorded for NPN at activation temperature of 500^{0}C, activation time of 1hour and acid impregnation ratio of 1.0.

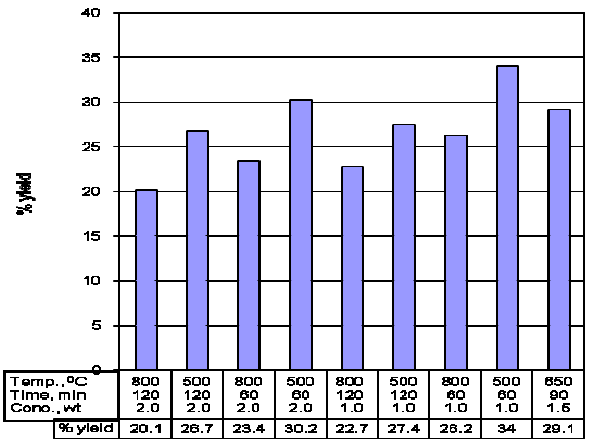

Figure-1
Percentage yield of NPN after carbonization

Characterization of activated carbon: Physico-chemical characteristics of activated carbon derived from nipa palm nut are shown in table-3. The values of fixed carbon , bulk density, surface area, volatile matter, iodine number were similar to the values obtained by Karthikeyan et al[18]. Vitidsant et al[15] produced activated carbon from palm oil shell and obtained yields of 12.18%, bulk density of 0.5048g/cm^3, 7.54% ash, iodine number of 766.99mg/g and 669.75m^2/g BET surface area.

Table- 3
Physico-chemical characteristics of activated carbon derived from nipa palm nut

Properties	Values
pH	6.9
Bulk density, g/cm^3	0.53
Iodine number, mg/g	815.62
Moisture content, %	4.8
Volatile matter, %	24.6
Ash content, %	3.88
Fixed carbon, %	71.52
Surface Area, m^2/g	871.22

Production of activated carbon using 2^3 full factorial experimental design: A 2^3 full factorial experimental design was employed to evaluate the preparation of activated carbon. The activation temperature and retention time plus the phosphoric acid /precursor impregnation ratio for the production of activated carbons were optimized based on the percentage removal of Pb^{2+} from aqueous solutions. The adsorption tests were used to analyze the best activated carbon for Pb^{2+} adsorption under different conditions of temperature, time and acid/precursor ratio.

Table-4
Minitab output for preparation of NPN based on Pb^{2+} adsorption

Predictor	Coefficient	StDev	T-value	P-value
Constant	125.664	2.280	55.13	0.000
Temp	-0.040012	0.002473	-16.18	0.000
Time	-4.7837	0.7418	-6.45	0.000
Conc	-1.4287	0.7418	-1.93	0.078
S = 1.484 R-Sq = 96.2% R-Sq(adj) = 95.3%				
Analysis of Variance				
Source	**DF**	**SS**	**MS**	**F-value**	**P-value**
Regression	3	676.06	225.35	102.40	0.000
Error	12	26.41	2.20	0.00	0.000
Total	15	702.47	0.00	0.00	0.000

Table -5
Experimental and Theoretical values for percentage removal of Pb^{2+}

Run	Temp	Time	Conc.	% Rem	Theoretical
1	800	1	1	88.23	87.44125
2	500	1	1	97.24	97.445
3	800	2	2	80.44	81.22875
4	800	2	1	83.07	82.6575
5	800	2	1	83.15	82.6575
6	800	1	2	86.06	86.0125
7	500	2	2	92.33	93.2325
8	800	2	2	79.98	81.22875
9	500	2	2	92.65	93.2325
10	800	1	2	85.82	86.0125
11	500	1	1	96.85	97.445
12	500	1	2	99.82	98.01625
13	500	1	2	99.88	98.01625
14	500	2	1	96.05	94.66125
15	800	1	1	87.93	87.44125
16	500	2	1	95.89	94.66125

The adsorption tests were performed at fixed parameters (contact time of 3hrs; initial ion concentration of 100mg/l; adsorbent dose of 0.5g; pH of 6 for Pb^{2+} and agitation speed of 200rpm). Minitab Release 11.21 was used for the statistical analysis. The result of the Minitab output is given in Table-4. Table-5 shows predicted values and experimental results for percentage removal of Pb^{2+}. It can seen that the optimum percentage removal, 99.88% for experimental and 99.016% for predicted values, was obtained for activated carbon produced at temperature of 500^0C, 1hr of activation and concentration of 1:2 (acid/NPN ratio, wt/wt %). The P values were used as a tool to check the significance of each of the coefficients, which in turn are necessary to understand the pattern of the mutual interactions between the test variables[19]. The regression equation is shown in equation 2

% Rem = 126 - 0.0400 Temp - 4.78 Time - 1.43 Conc ….2

P values, F values, T values, coefficient of determination, R^2 and adjusted coefficient of determination, R^2 (adj.) are given in table-4. The larger the magnitude of F-test value, and the smaller the P-values, the higher the significance of corresponding coefficient[20]. The fitness of the model equation was expressed by the coefficient of determination, R^2. R^2 indicates the fraction of the total variables of response variable that has been explained by the predicator variables. The greater the value of R^2, the better the fit and the more effective the estimated regression equation for estimation and prediction[21]. The greater the magnitude of a T-value, the greater the relative accuracy of estimating the corresponding coefficients. The result of the ANOVA cited in table-4 indicates that the linear model is adequate and the coefficients are significant except for concentration for Pb^{2+} adsorption on NPN at 5% level of significance. The contour and 3D surface plots for the production of activated carbons are shown in figures 2 and 3 respectively. The contour plots were studied to find optimum values of the combination of the independent variables. It is evident from figures-2 and 3 that decreasing the temperature and time of activation to 500^0C and 1hr respectively increased the percentage of Pb^{2+} adsorbed.

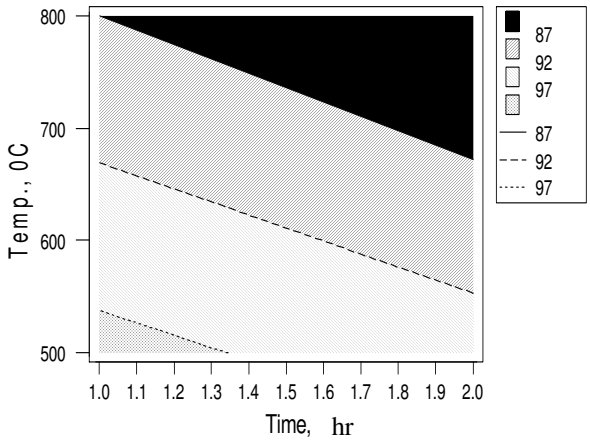

Figure-2
Contour plot for production of NPN using Pb^{2+} adsorption

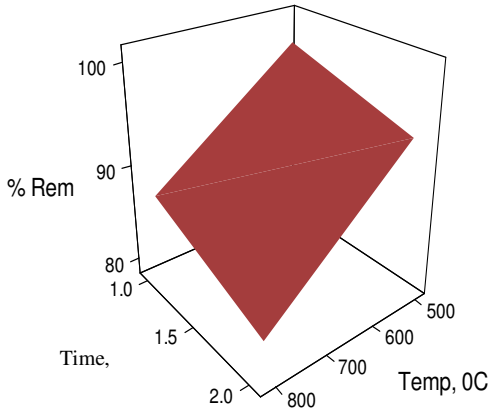

Figure-3
3D surface plot for production of NPN using Pb^{2+} adsorption

Isotherm studies: The equilibrium adsorption isotherm is important in the design of adsorption systems[22]. In general, the adsorption isotherm describes how adsorbate interact with adsorbents and this is critical in optimizing the use of adsorbents, The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm.

Langmuir isotherm model: The Langmuir adsorption model is given by

$$q_e = Q \frac{b\,C_e}{1 + b\,C_e} \qquad \text{…….3}$$

The Langmuir equation can be described by the linearized form[23, 24].

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \left(\frac{1}{Q_o}\right) C_e \qquad \text{……4}$$

The Langmuir constants, Q and b were evaluated from the intercept and the slope of the linear plot of experimental data of $^1/q_e$ versus $^1/C_e$ (figure-4) and presented in table-6. The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L[25].

$$R_L = \frac{1}{1 + bC_O} \qquad \text{……5}$$

Table- 6
Calculated Langmuir isotherm parameters for the adsorption of Pb^{2+} on NPN

	Temperature, K		
	303	313	323
Q (mg/g)	125	142.85	142.85
b (L/mg)	0.0620	0.0583	0.0625
R_L	0.1389	0.1464	0.1379
R^2	0.986	0.984	0.985

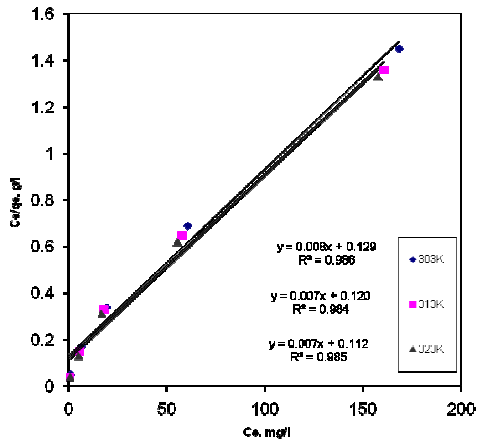

Figure-4
Langmuir isotherm for the adsorption of Pb^{2+} on NPN

Where, C_o is the initial ion concentration, b the Langmuir's adsorption constant (L/mg). The R_L value implies the adsorption to be unfavourable ($R_L > 1$), Linear ($R_L = 1$), favourable ($O<R_L<1$), or irreversible ($R_L=0$) (Maheswari et al, 2008). R_L values for Pb^{2+} on the NPN ranged from 0.984 to 0.986, indicating favourable adsorption under conditions used in this study. The correlation coefficients showed that Pb^{2+} adsorption on NPN follow Langmuir. Results obtained by some researchers showed that experimental data conformed to Langmuir model[26].

Conclusion

Activated carbon was prepared from nipa palm nut by chemical activation in phosphoric acid at different activating conditions. The quality of the carbon is dependent on the preparation condition. The optimum condition for preparing activated carbon for lead(11) removal from aqueous solution was obtained at activation temperature of 500^0C, activation time of 1hr and acid impregnation ratio of 1:2 (acid/precursor, wt basis). The experimental results obtained were in agreement with the model predictions. The adsorption data conformed to Langmuir isotherm equation.

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