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Production Of Activated Charcoal From Sugar Cane Leaves Using $ZnCl_2$ Activation For The Adsorption Of Methylene Blue Dye

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Abstract

This work explores the feasibility of sugar cane leaves, a biomass as an alternative precursor for preparation of activated carbon via Zinc Chloride activation. The effect of the operational parameters, chemical impregnation ratio, pyrolysis temperature on the carbon yield and methylene blue adsorption capability were investigated. In addition to this, physical characterization of the same was done to determine its surface area, bulk density, pore volume, ash content, moisture content and particle size distribution. It was found that adsorption capacity increases with increasing amount of activating agent and in terms of pyrolysis temperature, methylene blue number increases from 400^oC to 500^oC and sharply decreases after 500^oC up to 600^oC. The kinetic data fits very well with the first-order kinetic model. The Freundlich model showed higher correlation with the above experimental adsorption data.

Keywords: *Activated charcoal, sugarcane leaves, chemical activation, methylene blue number.*

1. Introduction

Most industries use dye and pigments to colour their products. More than 8000 chemically different types of dyes are being manufactured and the biggest consumers of these dyes are textile, tannery, and paper pulp industries and perhaps these are the serious polluters of our environment as far as colour pollution is concerned. Many dyes used in the textile industry are difficult to remove by conventional waste treatment methods since they are resistant to aerobic digestion. Presence of very minute concentration of colouring substance makes water unsuitable for several domestic applications. The removal of dyes from effluent in an economic fashion remains a major problem. Adsorption is the widely used technique for removal of dyes from aqueous solution. Carbon adsorption is one of the most dependable and efficient treatment process to provide high quality effluent. Several works has been reported in literature on colour removal from aqueous solution by carbon adsorption technique [6],[11]. In recent years, several investigations have concentrated their work on low cost, non-conventional materials to achieve the economically feasible and effective activated carbon like oil palm shell by chemical and physical activation[1], Bamboo charcoal[2], jack fruit peel waste by H_3PO_4 chemical activation[3], dates' stones activated by $ZnCl_2$ [4],[12], herb residues [5], cotton [6], Tectona grandis saw dust by $ZnCl_2$ activation[7], orange peel via microwave induced K_2CO_3 activation [8], coffee husks using $FeCl_3$ and $ZnCl_2$[9], Posidonia oceanica (L.) dead leaves[10], jute sticks [11], waste apricot [13].

India is an agricultural based country and huge amounts of wastes are being generated from agricultural operations. Hence, in the present study it is proposed to prepare activated charcoal from an agricultural byproduct such as sugar cane leaves using Zinc Chloride as the activating agent to determine their physico-chemical characteristics in order to find out whether this charcoal could be used as low cost adsorbent as alternative to commercial activated carbon in water and wastewater treatment process, especially for the removal of dyes.

2. Materials & Methods

2.1 Materials:

Sugar cane leaves were selected from the local farms. Zinc chloride ($ZnCl_2$) was procured from Merck, India and was used without further purification.

2.2 Preparation Methods of Activated Carbon:

Very first the material was shredded and oven dried at 120^{o}C for 1 hr. A typical chemical method was carried out for preparation of sugar cane leaves- based activated carbon. The process followed involves two steps namely, activation and pyrolysis. In activation step, dried sugar cane leaves with mass of 50 g were soaked in $ZnCl_2$ solution for 24 h at impregnation ratio (1:1, 1:0.5, and 1:0.1).

The soaked sugar cane leaves were dried in oven at 120^{o}C for 8-10 h and heated in muffle furnace at pyrolysis temperature (400, 500, 600^{o}C) for 2 h. After that, to the resultant three washings were given (cold water, 5 % HCl, hot water). Finally, the samples were dried in oven at 120^{o}C for 4-5 h and then crushed and sieved to obtain smaller particle size.

2.3 Characterisation of Activated Carbon Produced:

The specific surface area was measured by standard BET (Brunauer, Emmett, and Teller) technique. [Autosorb-1 Quantachrome instrument (U.S.A.)]. Specific pore volume was measured by subtracting the specific skeletal volume from the specific particle volume. Bulk density by poured apparent density method, particle size by using Newton's Sieve series, moisture content and ash content were estimated.

The adsorptive capacity of prepared active carbon samples was determined by Methylene blue value.

Table. 1: Characterization Of Activated Carbon

Physical properties		
Parameter	$ZnCl_2$ carbonized Char	CAC
Bulk density, gm/ml	0.3	0.4
Surface area, m^2/gm	741	900
Pore volume, cm3/gm	0.47	0.6
Particle size	0.106 μ– 0.090 μ	0.106 μ– 0.090 μ
Proximate analysis		
Moisture %	2%	2%
Ash %	6%	5%

Table. 2: Yield And Adsorption Characteristics Of Activated Carbon

Ratio (Raw material: Activating agent)	Temperature ^{0}C	%Yield	Methylene blue value *(mg/gm)*
1 : 1	600	28.68	90.3
1 : 0.5	600	36.44	77.7
1: 0.1	600	37.56	21
1 : 1	500	40.24	100.8
1 : 0.5	500	35.06	84.7
1: 0.1	500	29.64	35
1 : 1	400	43.06	77.7
1 : 0.5	400	40.42	35
1: 0.1	400	36.46	21

3. Results & Discussions

A number of experiments were carried out to study the effect of the parameters on activation. The major parameters that affect the quality of activated charcoal were pyrolysis temperature, impregnation ratio. Also, kinetics and adsorption isotherm were found.

3.1 Effect of Variation of Ratio of $ZnCl_2$/carbonized Char:

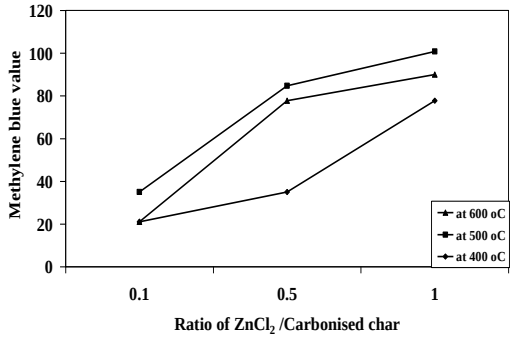

Fig .1 Effect of variation of the ratio of $ZnCl_2$/Carbonized char on Methylene Blue Value

It is observed that the adsorption power (Methylene blue value) of the carbon prepared, increases from 21 to 90.3 at 600°C, 35 to 100.8 at 500°C and 21 to 77.7 at 400°C with increase in $ZnCl_2$/char ratio(figure.1).

3.2 Effect of Variation of Activation Temperature on $ZnCl_2$ Carbonized Char:

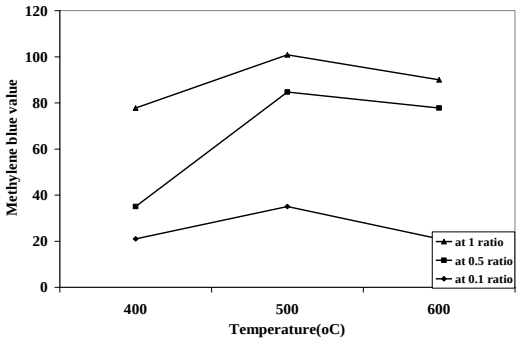

Fig.2 Effect of variation of activation temperature on $ZnCl_2$ based char on Methylene blue Value

It is observed that the methylene blue value of the prepared carbon increases from 21 to 35 at 1:0.1 ratio, 35 to 84.7 at 1:0.5 ratio , 77.7 to 100.8 at 1:1 ratio upto 500°C, reaches a maximum and then falls sharply to 21, 77.7 and 90.3 respectively, as the temperature was increased to 600°C. (Figure 2)

Activation was found to increase rapidly with temperature upto 500°C reaching a maximum value. The process of forming mesopore structure is till 500°C while these mesopores get converted into micopores above 500°C indicating a different mechanism of activation.

3.3 Adsorption Dynamics:

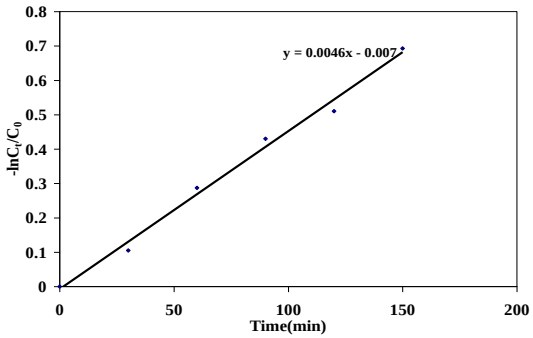

Fig.3 Adsorption dynamics ($ZnCl_2$, 500 °C, 1:1 ratio)

Kinetics modeling of the adsorption of dye by sugarcane leaves based activated carbon was found to best fitted to the first order kinetic model, as under.

$$-\ln C_t/C_0 = k_d t \qquad (1)$$

Where C_0 is the initial concentration, C_t is the concentration at any time and k_d is the rate constant. The values of rate constant are found to be 0.0046 min^{-1} for $ZnCl_2$ based char (figure.3) Since the plot of $-\ln C_t/C_0$) Vs t for sample activated carbons are linear, it is confirmed that the adsorption dynamics is of first order type.

3.4 Adsorption Isotherm:

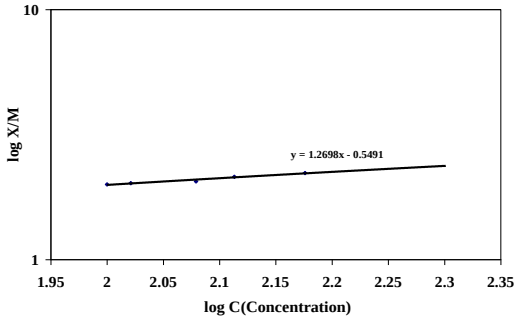

Fig.4. Adsorption isotherm of Methylene blue onto activated Carbon ($ZnCl_2$, 500 °C, 1:1 ratio)

In order to model the adsorption behaviour and to calculate the adsorption capacity of activated carbon, Freundlich adsorption isotherm was employed for adsorption equilibrium.

$$X/M = kC^{1/n} \qquad (2)$$

Where, X – amount of adsorbate adsorbed.
M – weight of carbon.
X/M – in the adsorbed phase i.e. amount of adsorbate adsorbed per unit weight of carbon.
C – equilibrium concentration of adsorbate in solution after adsorption
k and n are constants.

Taking logarithm on both sides of the equation,

$$\log (X/M) = \log k + {}^{1}/n \log C \qquad (3)$$

Linear plot of log (X/M) Vs log C (figure 4) shows that, adsorption follows Freundlich isotherm. Values of log k & 1/n were calculated from the intercepts and slopes of the plots. The values are log k = -0.5491, 1/n =1.2698 (i.e., n = 0.78, k = 0.2824) for $ZnCl_2$ sample (at 500 ^{0}C, 1:1 ratio).

3.5 Performance of Activated Carbon Samples:

Figure 5 shows that $ZnCl_2$/carbonized char [Ratio 1:1, temp. 500^{o}C] has higher adsorption capacity or decolourising power (100.8 mg/gm).

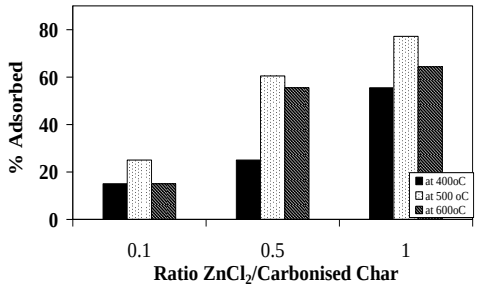

Fig.5. Performance of various Carbons ($ZnCl_2$ Samples)

4. Conclusions

The physico-chemical characteristics of prepared activated charcoal reveal that sugar cane leaves could be used as the raw material. As this material is disposed as agricultural wastes/byproducts, the activated charcoal is expected to be economical. Also activation catalyst like zinc chloride will provide a viable option to remove colour. The charcoal obtained under optimized carbonization conditions has a specific adsorptive power with respect to methylene blue value indicating its potential use as an adsorbent for removal of dye. The adsorption performance was found to vary with the activation agent/ char ratio and activation temperature. The adsorption follows Freundlich isotherm and the adsorption kinetics tend to follow first order kinetics.

References

[1]A.A.Niya, W.M.A. W.Daud, F.S. Mjalli, "Comparative study of the textural characteristics of oil palm shell activated carbon produced by chemical and physical activation for methane adsorption", *Chemical Engineering Research and Design*, *Vol. 89, Issue 6*, June 2011, Pages 657-664.

[2] D. Fu,Y.Zhang, F.Lv, P.l K. Chu, J. Shang, "Removal of organic materials from TNT red water by Bamboo Charcoal adsorption", *Chemical Engineering Journal*, *Vol.193–194*, 15 June 2012, Pages 39-49.

[3] D. Prahas, Y. Kartika, N. Indraswati, S. Ismadji, "Activated carbon from jackfruit peel waste by H_3PO_4 chemical activation: Pore structure and surface chemistry characterization", *Chemical Engineering Journal*, *Vol. 140, Issues 1–3*, 1 July 2008, Pages 32-42

[4] H. S. Bamufleh, "Single and binary sulfur removal components from model diesel fuel using granular activated carbon from dates' stones activated by $ZnCl_2$", *Applied Catalysis A: General*, *Vol. 365, Issue 2*, 31 August 2009, Pages 153-158.

[5] J.Yang, K.Qiu, "Development of high surface area mesoporous activated carbons from herb residues", *Chemical Engineering Journal*, *Vol. 167, Issue 1*, 15 February 2011, Pages 148-154.

[6] K.L.Chiu, D. H.L. Ng, "Synthesis and characterization of cotton-made activated carbon fiber and its adsorption of methylene blue in water

treatment", *Biomass and Bioenergy*, *Vol. 46*, November 2012, Pages 102-110.

[7] K.Mohanty, D. Das, M.N. Biswas , "Adsorption of phenol from aqueous solutions using activated carbons prepared from *Tectona grandis* sawdust by $ZnCl_2$ activation", *Chemical Engineering Journal*, *Vol.115, Issues 1–2*, 15 December 2005, Pages 121-131.

[8] K.Y. Foo, B.H. Hameed, "Preparation, characterization and evaluation of adsorptive properties of orange peel based activated carbon via microwave induced K_2CO_3 activation", *Bioresource Technology*, *Vol.104*, January 2012, Pages 679-686.

[9] L. C.A. Oliveira, E.Pereira, I. R. Guimaraes, A.Vallone, M. Pereira, J.P. Mesquita, K.Sapag, "Preparation of activated carbons from coffee husks utilizing $FeCl_3$ and $ZnCl_2$ as activating agents", *Journal of Hazardous Materials*, *Vol. 165, Issues 1–3*, 15 June 2009, Pages 87-94.

[10] M. U. Dural, L. C., S. K. Papageorgiou, F. K. Katsaros, "Methylene blue adsorption on activated carbon prepared from *Posidonia oceanica* (L.) dead leaves: Kinetics and equilibrium studies", *Chemical Engineering Journal*, *Vo. 168, Issue 1*, 15 March 2011, Pages 77-85.

[11] M. Asadullah, M. Asaduzzaman, M. S. Kabir, M. G. Mostofa, T.Miyazawa, "Chemical and structural evaluation of activated carbon prepared from jute sticks for Brilliant Green dye removal from aqueous solution", *Journal of Hazardous Materials*, *Vol. 174, Issues 1–3*, 15 February 2010, Pages 437-443.

[12] S.K.Theydan, M.J.Ahmed, "Optimization of preparation conditions for activated carbons from date stones using response surface methodology", *Powder Technology*, *Vol. 224*, July 2012, Pages 101-108.

[13] Y. Önal, C. Akmil-Başar, Ç. Sarıcı-Özdemir, "Elucidation of the naproxen sodium adsorption onto activated carbon prepared from waste apricot: Kinetic, equilibrium and thermodynamic characterization", *Journal of Hazardous Materials*, *Vol. 148, Issue 3*, 30 September 2007, Pages 727-734.