

Preparation and Characterization of Activated Carbon from Casuarina for the Removal of Dyes from Textile Wastewater

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Abstract: Activated Carbon of high adsorption capacities were prepared from Casuarina by various physical and chemical processes like dolomite process, direct pyrolysis, impregnation of raw material with Conc.H₂SO₄, H₃PO₄, KOH, Na₂SO₄, Na₂CO₃ and ZnCl₂ solution followed by the activation at 800°C. Adsorption capacity of activated carbon is due to the porous structure, chemical nature of the surface and pH of the aqueous solution. The physico-chemical characteristics such as moisture content, volatile content, Specific gravity, Porosity, bulk density, pH, conductivity, Methylene blue number, iodine number were also investigated in order to understand the adsorptive capacity of activated carbon prepared from the agricultural wastes. Based on the results obtained from the characterization studies, the activated carbon prepared by impregnation with H₃PO₄ (10 %) solution followed by activation at 800°C was selected as the best adsorbent due to the highest surface with large number of pores and low ash content for the removal of dyes from industrial effluent. Experimental results indicated that the activated carbon prepared by H₃PO₄ impregnation is best suitable for the removal of synthetic dyes from effluents.

Keywords: Adsorption, H₃PO₄ impregnation, Activated carbon, characterization, effluents.

Introduction

Environmental pollution due to industrial effluents is of major concern because of their toxicity and threat for human life and the environment. The discharge of textile effluents to the water bodies has raised much concern because of potential hazards associated with the entry of toxic components into the food chains of humans and animals. Synthetic dyes are extensively used for dyeing and printing in a variety of industries. Dyes are used in many industries such as carpets, paper, plastics, food and textile in order to colour their products¹. Over 10,000 dyes with an annual production over 7x10⁵ metric tons worldwide are commercially available and 5-10% of the dye stuff is lost in the industrial effluents². Therefore there is a need to remove dyes before effluent is discharged into receiving water bodies. The most popular treatment methods for textile wastewater are combinations of biological treatment, chemical coagulation, chemical oxidation, membrane separation, electrochemical treatment, filtration, hydrogen peroxide catalysis, reverse osmosis and activated carbon adsorption³⁻⁵.

Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, use of operation and insensitivity to toxic substances⁶. Adsorption has been used extensively in industrial process for separation and purification. The removal of coloured and colourless organic pollutants from industrial wastewater is considered as an important application of adsorption processes. Adsorption by activated carbon has a greater tendency for the removal of dyes without introducing any impurities. The advantage of activated carbon materials as adsorbents is that the treated effluent is of high quality, the design of the process is so simple, and the operation of the process developed is easy. In addition, carbon materials are resistant to corrosive and toxic environments⁷. The demand for activated carbon is increasing owing to the increased utility of the carbon materials in pollution control. As a result, cost of activated carbon is also growing depending on the application. Designing ways for the production activated carbon through economic ways is the need of the hour. A range of low cost, easily available, carbon rich and low ash precursors and sources are being explored for the production of carbon materials.

As the applications of activated carbon are immense, the gap between demand and supply is ever widening. This may in due course result in scarcity of the material in addition to becoming expensive. This situation necessitates the need for the exploration of new sources of carbon materials with desired physico chemical properties namely high surface area, micro or meso porosity, thermal stability, surface functionality, carbon purity and adsorptive capacity. Adsorption by activated carbon is proven to be very effective in treating textile wastes.

However, in view of the high cost and associated problems of regeneration, there is a constant search for alternate low cost adsorbents⁸. This difficulty has led to search for the use of cheap and efficient alternative materials such as rice husk⁹, bamboo¹⁰, sugarcane stalks¹¹, tamarind kernel powder¹², palm shell¹³, babool wood¹⁴, baggase flyash¹⁵, ashoka leaf powder¹⁶, coir pith¹⁷, banana pith¹⁸, etc. The preparation of activated carbon with different pore sizes can be achieved by physical or chemical activation processes. In both methods, the development of porosity is different in terms of practical procedures and mechanism. Physical activation refers to the carbonization of precursor material followed by activation of the resulting char in presence of N₂, CO₂ and steam.

In Chemical activation process, the precursor is mixed with chemicals such as chloride salts, sulphate salts, carbonate salts, KOH, HCl, H₂SO₄, H₃PO₄, etc. and they are carbonized and washed to produce activated carbon. Following the thermal decomposition of the precursor, the chemical reacts with the product causing reduction in the evolution of volatile matter and inhibition of the particle shrinkage. Once the chemical is removed by exhaustive washing, a large amount of porosity is formed. Chemical activation has more advantages over physical activation with respect to higher yield, more surface area, and better development of porous structure, oxygenated surface complexes in carbon.

The main objective of this work is to investigate the preparation of activated carbon from the char obtained by gasification of the seeds and branches of casuarina and to find the optimum conditions for making activated carbon with well developed porosity and high surface area which can be used effectively for the removal of dyes from wastewater.

Materials And Methods

The seeds and branches of Casuarina were collected and cut into small pieces (2 cm), washed with distilled water, dried in sunlight for 10 days and stored to prepare the activated carbons by both physical and chemical methods. The activated carbons were powdered, characterized using physico chemical methods and used for adsorption studies¹⁹.

Carbonization procedures²⁰

The activated carbon were prepared by the following method and listed in Table 1.

Table 1 List of Activated carbons prepared from agricultural wastes

S.No	Activated carbon	Preparation method
1.	CAC1	Direct Pyrolysis
2.	CAC2	CaCl ₂ impregnation
3.	CAC3	Na ₂ SO ₄ impregnation
4.	CAC4	Na ₂ CO ₃ impregnation
5.	CAC5	H ₃ PO ₄ impregnation
6.	CAC6	HCl process
7.	CAC7	H ₂ SO ₄ process
8.	CAC8	KOH impregnation
9.	CAC9	Dolomite process

Direct pyrolysis

The precursor material was subjected to carbonization at 400 °C, powdered well and finally activated at a temperature of 800° C for a period of 10 minutes. After activation, the material was repeatedly washed with plenty of distilled water.

Carbonization with CaCl₂

The material to be carbonized was impregnated with a boiling solution of 10% CaCl₂ for 2 hours and soaked in the same solution for 24 hours. At the end of 24 hours, the excess solution was decanted off and air dried. Then the material was carbonized in muffle furnace at 400 °C. The dried material was powdered and activated in a muffle furnace at 800° C for a period of 10 minutes. Then the material was washed with plenty of water to remove residual acid, dried and powdered.

Carbonization with Sulphate salts

The precursor material was soaked in 10% solution of sodium sulphate for the period of 24 hours. After impregnation, the liquid portion was decanted off and then dried. The dried mass was then subjected to carbonization process in a muffle furnace at 400 °C. The dried material was powdered and activated in a muffle furnace at 800° C for a period of 10 minutes. Carbonization with Carbonate salts

The material to be carbonized was soaked in 10% solution of Calcium carbonate for 24 hours. At the end of 24 hours, the excess liquid portion was decanted off and air dried. The dried mass was then subjected to carbonization process in a muffle furnace at 400 °C. The dried material was powdered and activated in a muffle furnace at 800° C for a period of 10 minutes.

Carbonization with H₃PO₄

The precursor material was impregnated with boiling solution of 10% H₃PO₄ for 2 hours and soaked in the same solution for 24 hours. At the end of 24 hours, the excess solution decanted off and air dried. Then the material was carbonized in muffle furnace at 400 °C. The dried material was powdered and activated in a muffle furnace at 800° C for a period of 10 minutes. Then the material was washed with plenty of water to remove residual acid, dried and powdered.

Carbonization with KOH

The dried precursor material was soaked with 10% KOH solution for 24 hours. At the end of 24 hours, the excess KOH solution was decanted off and air dried. Then the material was subjected to carbonization process in a muffle furnace at 400 C400 °C for 2 hours. The dried material was powdered and activated in a muffle furnace at 800° C for a period of 10 minutes. After activation, the carbon was washed with 4N HCl to remove the residual KOH. Then the material was washed with plenty of water, dried and stored.

Acid process

The dried material was treated with excess of hydrochloric acid and sulphuric acid respectively. Charring of these materials occurred immediately, accompanied by evolution of heat and fumes. When the reaction subsided, the mixture was left in an air oven maintained at 140-160 °C for a period of 24 hours. At the

end of this period, the product was washed with large volume of water to remove free acid, dried at 110 °C and finally activated at 800° C.

Dolomite Process

The dried material which is to be carbonized was taken over calcium carbonate bed and the upper layer of the precursor was also covered with a layer of calcium carbonate. The entire material was carbonized at 400 °C, powdered well and then was activated at 800° C. After activation, the material was washed with excess of water to remove calcium carbonate and dried at 110° C.

Characterization of the carbons

Conductivity and pH were analyzed using Elico make pH meter (model L1-120) and conductivity meter (model M-180) respectively. Moisture content (%) by mass, ash content (on dry basis) % by mass, volatile matter, fixed carbon content, bulk density, Specific gravity, Porosity, Iodine number, Methylene Blue number, matter soluble in water, matter soluble in acid were analyzed as per standard procedures and the values are listed in Table 2.

Table 2- Physico-chemical characteristics of agricultural wastes on activated carbon

S. No	Properties	Activated Carbon								
		AC1	AC2	AC3	AC4	AC5	AC6	AC7	AC8	AC9
1	pH	6.74	6.41	7.25	8.45	6.87	7.31	7.18	8.23	7.80
2	Conductivity, mS cm ⁻²	0.38	0.29	0.42	0.54	0.12	0.25	0.25	0.19	0.26
3	Moisture content, %	10.18	15.44	15.19	16.07	16.30	14.24	18.23	25.51	18.80
4	Ash, %	17.4	18.6	11.6	16.1	10.3	15.2	16.6	12.6	14.8
5	Volatile matter, %	13.3	6.6	10.6	11.3	5.7	12.6	7.3	18.2	11.3
6	Matter soluble in water, %	0.48	0.33	0.21	0.25	0.19	0.48	0.51	0.42	0.53
7	Matter soluble in 0.25 M HCl, %	1.23	0.98	0.85	1.04	0.80	1.15	1.18	1.33	1.56
8	Bulk density, g mL ⁻¹	0.27	0.28	0.29	0.35	0.42	0.30	0.37	0.38	0.33
9	Specific Gravity	1.24	1.46	1.56	1.65	1.87	1.43	1.10	1.05	0.88
10	Porosity, %	78.22	74.57	80.24	81.30	75.15	79.09	66.45	63.87	27.14
11	Methylene Blue Number, mg g ⁻¹	450	255	195	165	525	150	115	375	154
12	Iodine Number, mg g ⁻¹	977.3	1074.5	1079.5	1103.2	1186.9	1084.5	1065.8	1078.2	1059.5
13	Fixed Carbon, %	59.12	59.36	62.61	56.53	67.7	57.96	57.87	43.69	57.1
14	Yield, %	52.7	41.2	55.2	56.1	69.2	58.3	57.4	59.5	52.3

Dye Adsorption Studies:

In this part of study, 0.2g of adsorbent was agitated with 50 ml of 50 ppm dye solution for a period of 2 hours. Finally the supernatant solution was filtered using whattman filter paper No.41 and analyzed spectrometrically using Elico U.V. Visible Spectrometer (Model BL 192) for residual dye concentration.

Results and Discussion

The pH of AC1, AC2, AC3, AC5, AC6 and AC7 are near neutral which will be helpful for the treatment of all types of dyes and wastewater. The carbon obtained could also be used for the purification of drinking water. AC4, AC8 and AC9 carbons are found to be slightly basic in nature. This may be due to the presence of residual salts in the carbon. No marginal variation was noticed in the conductivity values of carbons prepared in all the processes. This may be due to the presence of uniform exchangeable site on the porous surface of the activated carbon.

From Table 2, the moisture content was found to be higher in the case of carbons obtained by KOH and dolomite process. Even though moisture content of the carbon has no effect on its adsorptive power, it dilutes the carbon which necessitates the use of additional weight of carbon during treatment process. Ash content generally gives an idea about inorganic constituents associated with carbon obtained by different carbonization methods²¹. The ash content values from Table 2. indicate that the overall ash content for all varieties of carbon prepared shows a comparable lesser value. This may be attributed to lower inorganic content and higher fixed carbon.

Volatile matter is due to the presence of highly porous organic compounds present in the raw material. High value of ash and volatile matter reduces the quantity of fixed carbon. From the data it was clear that all carbons have a good percentage of fixed carbon. Solubility studies of carbon in acid and water were performed to evaluate the amount of impurities present in the carbon prepared by different carbonization process. The solubility studies were performed since the presence of impurities in the carbon may affect the expected quality of the treated water during treatment. From Table 2, the data pertaining to the matter soluble in water and acid indicates that all carbons contain very less amount of impurities.

Porosity is the main factor for increasing the adsorptive power of an activated carbon. Porosity is also interrelated to the bulk density and specific gravity of activated carbon. From Table 2, it is clearly seen that AC5 has higher porosity than all the other carbons. Bulk density indicates the fibre content present in the precursor material. From the data's shown in Table 2, it is indicated that all the nine carbons have relatively equal bulk density.

Methylene blue number is an indication of the ability of a carbon to adsorb high molecular weight substances like dye molecules. From table 2, AC5 shows higher Methylene blue number of greater than 400, which indicates that, the carbon is very effective for the removal of dyes. Iodine number is the most fundamental parameter used to characterize the performance of an activated carbon. It is a measure of the activity level which is often reported in mg/g. It is a measure of micropore content of the activated carbon by adsorption of iodine from solution. It is equivalent to the surface area of carbon between 900 m²/g and 1100 m²/g. From Table 2, it is clear that AC5 has higher iodine number indicating that it is best suitable for dye removal.

In all the processes, the final carbon yield from Table 2 shows encouraging results. AC5 has higher yield when compared to the yields of all other carbons. This shows that AC5 is best suited activated carbon of higher porosity which could be very effective in the field of adsorption.

Scanning Electron Microscope

Examination of SEM micrographs (Fig 1.1 to 1.9) of activated carbon particles shows smooth areas having long ridges and rough areas with mesopores and more number of edges. An electron microscope study reveals highly porous and branched particles particularly in CAC3, CAC5, CAC6, CAC7, CAC8 and CAC9. Small cavities, pores and more rough surfaces on the carbon sample indicate the presence of interconnected porous network. SEM photograph of CAC5 shows that the surface is pitted and fragmented due to the carbonization with H₃PO₄ acid and activation process. The surface area of CAC5 is found to be enhanced by the presence of more porosity, which can hold more solute from solution during adsorption.

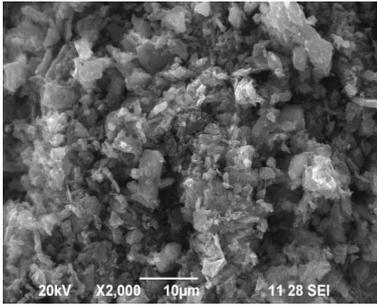


Figure 1.1.SEM image of CAC1

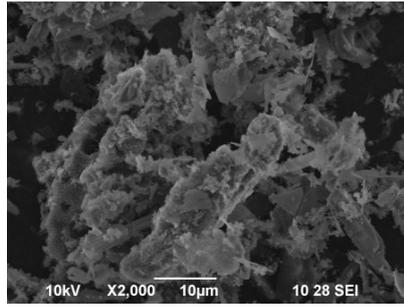


Figure 1.2. SEM image of CAC2

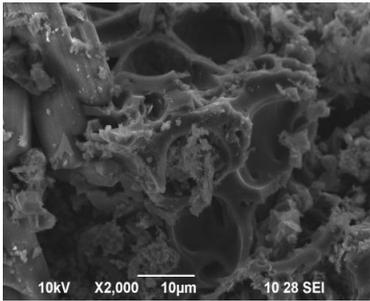


Figure 1.3.SEM image of CAC3

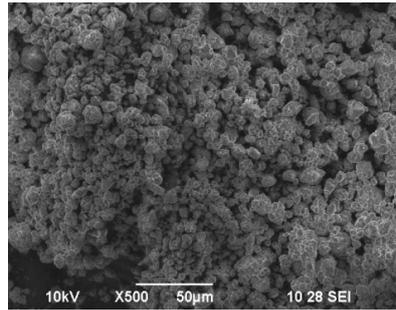


Figure 1.4. SEM image of CAC4

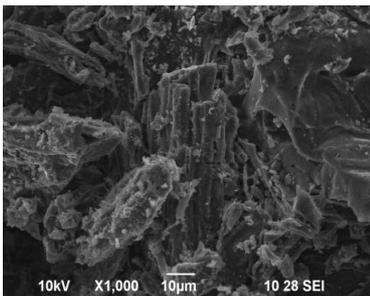


Figure 1.5.SEM image of CAC5

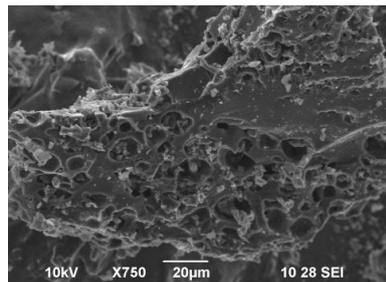


Figure 1.6. SEM image of CAC6

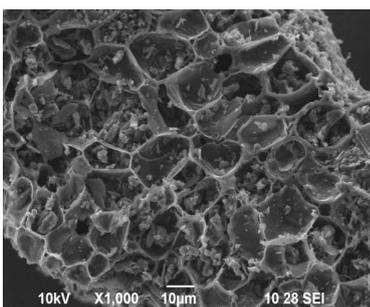


Figure 1.7.SEM image of CAC7

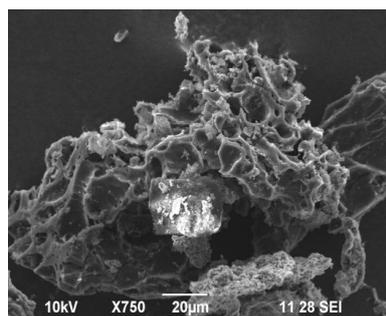


Figure 1.8. SEM image of CAC8

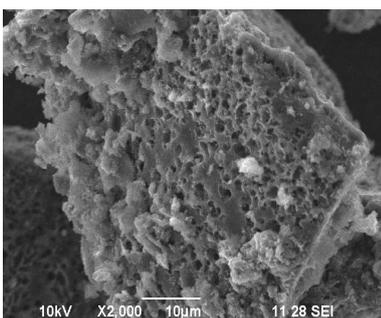


Figure 1.9. SEM image of CAC9

X-ray Diffraction Studies

Details of phase structure and the process of graphitization of carbon materials were obtained from XRD studies. The broadness of the peaks indicates the amorphous nature of the carbon. Several sharp and intense diffraction peaks were also observed in the XRD profile and they are the result of silica and other typical mineral matter present in the plant tissues which remain intimately bound with carbon material.

Conclusion

From the results of the present investigation, it can be concluded that,

- i) Activated carbon can be conveniently and economically prepared from casuarina wood.
- ii) The extensive characterization studies of different varieties of activated carbon reveal that the phosphoric acid impregnated carbon can be assessed as superior grade carbon.
- iii) Iodine number which is a measure of micropore content of the activated carbon reveals that the carbon obtained from phosphoric acid impregnation can be considered as the one with higher surface area and hence greater adsorption.
- iv) Porosity plays a major role in the selected adsorbent – adsorbate system.
- v) Hence the activated carbons obtained from casuarina can be used for the removal of dyes from the textile wastewater.

References

1. HajiraFahir, Muhammad Sultan and QaziJahanzeb., African Journal of Biotechnology, 2008, 7(15), 2649-2655.
2. Mohan.D.Singh, Singh,G. and Kumar., Ind.Eng.Chem. Res, 2002, 41, 3688-3695.
3. Juang, R.S.Tseng, R.L.Wu, F.C.and Lee, S.H., J.Chem.Technol.Biotechnol,1997,70, 391-399.
4. Madhavakrishnan.S, Manickavasagam.K., Vasanthakumar.R., Rasappan.K., Mohanraj.R and Pattabhi. S, E-Journal of Chemistry, 2009, 6(4), 1109-1116.
5. Khokhlova.T.D., Nikitin.Y.S. and Detistova. A.L., Adsorption Science and Technology, 1997, 15(5), 333.
6. Nwabanne.J.T, and Mordi. M.I., African Journal of Biotechnology, 2009,8 (8), 1555-1559.
7. Michal Kruk, Bruno dufour, Ewa.B. Celer, Tomasz Kowalewski, MietekJaroniec and Krzysztof Matyjaszewski., J.Phys.Chem.B, 2005, 109, 9216-9225.
8. Guptha.V, Agarwal.J, Purohit. M.andVeena., Res J Chem environ, 2007, 11, 40-43.
9. Adinata.D, Ashri.W. M, Daud.W.andAroua.M.K., Boirestechnol, 2007,98,145-149.
10. Sathish.M, Vanraj.B, Chauhan and Manocha.L.M., Carbon Sci, 2002,3, 133-141.
11. Milam M. Lakdawala and B.N.Oza., Advances in Applied Science Research, 2011, 2(4), 244- 251.
12. Ratna S. Shelke, Jagadish.V,Bharada, Balaji. R, Madje and Milind. B, Ubalea., Advances in Applied Science Research, 2011, 2(4), 6-11.
13. Ash.B, Satapathy. D, Mukherjee. P.S, Nanda.B,Gumasthe.J.L. and Mishra. B.K., Journal of Scientific and industrial research, 2006, 65, 1008 – 1012.
14. Shanmugham Arivolia, Thenkuzhalib.M and Martin Deva Prasath.P., The Electron Journal of Chemistry, 2009, 1(2), 138-155.
15. Ponnusamy Sivakumar and Nachimuthu Palanisamy., Advances in Applied Science Research, 2010, 1 (1), 58-65.
16. Joseph.T. Nawabne and Philomena.K.zlgbokwe., Advances in Applied Science Research, 2011, 2 (6), 166-175.
17. American Society for Testing Materials (ASTM), Estander test method for determination of Iodine Number of Activated carbon 4607-94, ASTM, 1980.
18. Brunauer.S, Emmett.P.H, and Teller.E., J.Am.Chem.Soc., 1938, 60, 309-315.
19. Yang.T, and Lua.A.C., Micropor Mater, 2003, 63, 113-124.
20. ISI, Activated Carbon, Powdered and granular – Methods of sampling and its tests, (Bureau of Indian Standards, New Delhi), IS 877 – 1989.
21. Raffieabaseri.J., Palanisamy.P.N., and Sivakumar.P., Advances in Applied Science Research, 2012, 3 (1):377-383.