

Preparation and characterization of activated carbon from *Thevetia peruviana* for the removal of dyes from textile waste water

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ABSTRACT

Activated Carbon (TPAC) of high adsorption capacities and highly active surface properties were prepared from *Thevetia peruviana* by physical and chemical processes such as direct pyrolysis, dolomite process, Chemical activation with $H_2SO_4 + H_2O_2$, impregnation of raw material with Conc. H_2SO_4 , KOH, $ZnCl_2$ and H_3PO_4 solution respectively followed by activation at $800^\circ C$. Adsorption capacity of activated carbon is due to porous structure, chemical nature of the surface and pH of the aqueous solution. The physico chemical characteristics such as moisture content, volatile matter, pH, conductivity, bulk density, specific gravity, porosity, methylene blue number, iodine number and SEM were investigated to understand the adsorptive capacity of activated carbon prepared from TPAC. Based on the results of the characterization studies, the activated carbon prepared by impregnation of TPAC with H_3PO_4 (30%) solution followed by activation at $800^\circ C$ was selected as a best quality adsorbent due to highest surface area with large number of pores and low ash content for the removal of dyes from textile industry effluent. The experimental results indicated that the prepared activated carbon is suitable for the removal of synthetic dyes from textile industry effluents.

Keywords: *Thevetia peruviana*, Adsorption, H_3PO_4 impregnation, Activated Carbon, Dye removal.

INTRODUCTION

In recent years, the pollution of water due to dyes becomes a great threat to the world, spreading critical diseases due to discharge of dyes. Dyes are used in many industries such as carpets, plastics, cosmetics, paper, food and textile in order to colour their products [1]. The World Bank estimates that 17 to 20 percent of industrial water pollution comes from textile dyeing and treatment. Discharge of dyes into rivers from these industries cause severe problems, as dyes gives toxicity to the aquatic life and also damaging the aesthetic nature of the environment [2]. Various methods of dye removal including aerobic and anaerobic microbial degradation, coagulation, chemical oxidation, membrane separation, electrochemical treatment, filtration, floatation, hydrogen peroxide catalysis, reverse osmosis and adsorption have been proposed from time to time.

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 substances [3]. Adsorption by activated carbon has a greater potential for the removal of dyes without introducing any impurities. However, these processes are effective and economic only in cases where concentrations of solute are relatively high. Adsorption onto 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 adsorbents [4].

This difficulty has led to search for the use of cheap and efficient alternative materials such as rice husk [5], bamboo [6], sugarcane stalks [7], tamarind kernel powder [8], palm shell [9] babool wood [10], bagasse fly ash [11], ashoka leaf powder [12], coir pith [13] and banana pith [14] etc. The preparation of activated carbon with different pore sizes can be achieved by physical or chemical activation process. In both methods, the development of porosity is different in terms of practical procedures and mechanism. In physical activation the generation of porosity took place via selective elimination of the more reactive carbon of the structure and further gasification led to the production of the activated carbon with high porosity.

In chemical activation process, the precursor is mixed with a chemical such as sulphate salts, chloride salts, KOH, HCl, $ZnCl_2$, H_2SO_4 , H_3PO_4 carbonized and washed to produce the 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.

The main objectives of this work is to investigate the preparation of activated carbon from a char obtained by gasification of wood of *Thevetia peruviana* and to find the optimum conditions for making activated carbon with well-developed porosity and high surface area. *Thevetia peruviana* (Pers.) K. Schum. (Commonly known as Yellow oleander) is an ornamental plant which grows in Kenya and other parts of the World, such as tropical America, Western Asia, Southern Europe, India and tropical Africa. This plant is the plant widespread throughout India and it does not have any economical importance.

MATERIALS AND METHODS

Thevetia peruviana wood were cut into small pieces (2cm), 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 studies [15].

2.1 Carbonization procedures [16]:

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

Table 1: List of Activated Carbons of *Thevetia peruviana* wood

S.No	Activated carbon	Preparation method
1.	TP1	Direct Pyrolysis
2.	TP2	Na_2SO_4 impregnation
3.	TP3	H_3PO_4 impregnation
4.	TP4	$ZnCl_2$ impregnation
5.	TP5	KOH impregnation
6.	TP6	HCl process
7.	TP7	H_2SO_4 process
8.	TP8	Dolomite process
9.	TP9	$H_2SO_4 + H_2O_2$ process

2.1.1 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 the activation, the material was repeatedly washed with plenty of distilled water.

2.1.2 Carbonization with sulphate salts

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

2.1.3 Carbonization with H_3PO_4

The material to be carbonized is impregnated with a boiling solution of 30 % H_3PO_4 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 [17].

2.1.4 Carbonization with $ZnCl_2$

The material to be carbonized is impregnated with a boiling solution of 10 % $ZnCl_2$ 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.

2.1.5 Carbonization with KOH

The dried material is soaked with 10 % KOH solution for 24 hours. At the end of 24 hours, the excess KOH solution decanted off and air dried. Then the material carbonized in muffle furnace at 400°C for 30 minutes. The carbon was powdered and activated in a muffle furnace at 800°C for a period of 10 minutes. After the activation, the carbon was washed sufficiently with 4N HCl to remove the residual KOH. Then the material was washed with plenty of water, dried and stored.

2.1.6 Acid process

The dried material was treated with excess of sulphuric acid and hydrochloric acid respectively. Charring of the material 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.

2.1.7 Dolomite process

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

2.1.8. Chemical activation with $H_2SO_4 + H_2O_2$

In this method, one part of the material and 1.5 parts of H_2SO_4 were mixed with 0.4 parts of H_2O_2 and kept in muffle furnace at 120°C for 12 hours. At the end of this period, the product was washed with large volume of distilled water to remove free acid, dried at 110°C and finally activated at 800°C.

2.2 Characterization studies:

Moisture content (%) by mass, Ash content (%) by mass, Bulk density, Specific gravity, Porosity, Iodine number, Methylene Blue number, pH, Conductivity, Matter soluble in acid, Matter soluble in water were analyzed as per standard procedures [18] & [19] for TPAC and the values were listed in Table 2. The Morphological characteristics of the samples were studied using Scanning Electron Microscope (SEM) (Make -Jeol, Model 6390LA).

RESULTS AND DISCUSSION

3.1 General Properties

The pH of TP1, TP3, TP4, TP6, TP7 and TP9 are near neutral which will be helpful for the treatment of all classes of dye waste water and the carbon can also be used for drinking water purification. TP2, TP5 and TP8 carbon are basic in nature, this may due to the presence of residual salts in the carbon. Conductivity values do not shows much

variation, this means that cations in acidic carbons and anions in basic carbons may be responsible for the conductivity.

Even though moisture content of the carbon has no effect on its adsorptive power, it dilutes the carbon and necessitates the use of additional weight carbon during treatment process. TP3 has low moisture content comparing to other carbon. Any porous material will have the tendency to absorb moisture. The moisture content of all the carbons are near normal and comparable with the values reported elsewhere [15].

Ash content shows the amount of inorganic substituents present in the carbon. From Table 2, it was found that all activated carbons have less ash content which can increase the fixed carbon value.

Volatile matter is due to the presence of organic compounds present in the raw material. From the data it was clear that all carbons have a good percentage of fixed carbon.

Water soluble matter and acid soluble matter give the information about the amount of impurities present in carbon which affect the quality of water. But in our analysis, the data show that all the carbons contain very low amount of impurities.

Porosity is the main factor for increasing the adsorptive power of an activated carbon. Porosity is related to the bulk density and specific gravity of activated carbon. TP3 has higher porosity than other carbons. TP3 has higher surface area of $862.39 \text{ m}^2 \text{ g}^{-1}$ showed that it is the highly porous carbon compared to other activated carbons.

Bulk density indicates the fibre content of the precursor. From the data it is shown that all nine carbons have relatively equal bulk density. Generally, an adsorbent with bulk density need not be regenerated frequently because it can hold more adsorbate per unit weight [20].

Methylene blue number is an indication of ability of a carbon to adsorb high molecular weight substances like dye molecule. TP3 shows methylene blue number of greater than 400, indicates that the carbon is good for dye adsorption.

Table 2: Physico-chemical Characteristics of *Thevetia peruviana* wood activated carbon.

S.No	Properties	Activated Carbon								
		TP1	TP2	TP3	TP4	TP5	TP6	TP7	TP8	TP9
1	pH	6.89	8.12	6.78	6.61	8.32	7.11	6.74	7.43	6.92
2	Conductivity, mS cm^{-2}	0.298	0.492	0.145	0.179	0.257	0.312	0.252	0.398	0.512
3	Moisture content, %	18.9	15.9	13.2	18.5	17.9	14.8	15.6	17.8	19.2
4	Ash, %	11.6	12.8	10.7	14.3	15.7	18.5	12.8	16.3	17.8
5	Volatile matter, %	21.8	25.9	20.9	23.6	24.5	22.3	23.7	19.8	21.7
6	Matter soluble in water, %	0.41	0.38	0.28	0.32	0.41	0.42	0.39	0.29	0.31
7	Matter soluble in 0.25 M HCl, %	1.31	0.94	0.94	0.89	0.82	1.35	0.87	1.21	1.05
8	Bulk density, g mL^{-1}	0.41	0.48	0.42	0.44	0.38	0.42	0.45	0.45	0.38
9	Specific Gravity	0.80	0.87	0.92	0.85	0.81	0.71	0.86	0.85	0.78
10	Porosity, %	48.75	44.83	54.35	48.24	53.09	40.85	47.67	47.06	51.28
11	Methylene Blue Number, mg g^{-1}	186	152	532	98	159	110	89	132	98
12	Iodine Number, mg g^{-1}	190	425	798	422	423	230	412	315	285
13	Fixed Carbon, %	47.7	46.2	55.2	43.6	41.9	44.4	47.9	48.7	41.6
14	Yield, %	47.2	51.5	58.6	47.6	52.72	53.4	48.90	48.7	41.4
15	Surface area(BET), $\text{m}^2 \text{ g}^{-1}$	329.27	205.63	862.39	503.77	561.096	156.24	390.69	85.93	299.85

Iodine number is the most fundamental parameter used to characterize activated carbon performance. It is a measure of activity level (higher number indicates higher degree of activation), often reported in mg/g (typical range 500–1200 mg/g). It is a measure of the micropore content of the activated carbon (0 to 20 Å, or up to 2 nm) by adsorption

of iodine from solution. It is equivalent to surface area of carbon between 900 m²/g and 1100 m²/g. From Table 2, it was clear that TP3 has higher Iodine number, indicating that it is best suitable for dye removal.

The values of yield from Table 2 show that TP3 has higher value when compared to other carbon. By comparing the data obtained from characterization studies, TP3 is suitable for preparing the activated carbon of high porosity.

3.2 Scanning Electron Microscope

SEM micrographs (Fig 1A to 1I) of activated carbon particles showed cavities, pores and more rough surfaces on the carbon samples. Granular pores and cavities will increase the surface area of the adsorbent. SEM photograph of TP3 shows that the surface is pitted and fragmented due to the carbonization with H₃PO₄ acid and activation process. The surface area of the TP3 will be enhanced by the presence of more porosity, which can hold more solute from solution during adsorption.

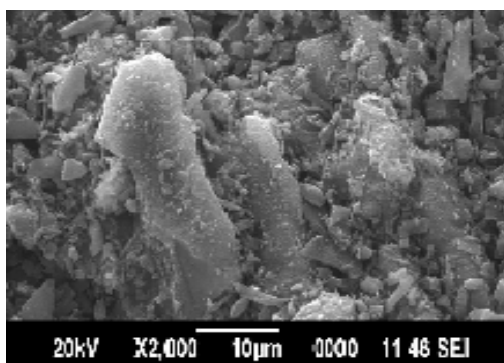


Fig. 1A SEM photograph of TP1 (2000 X)

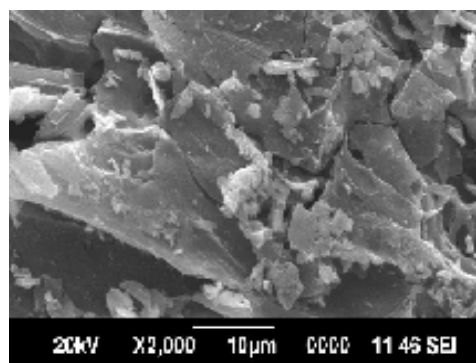


Fig. 1B SEM photograph of TP2 (2000 X)

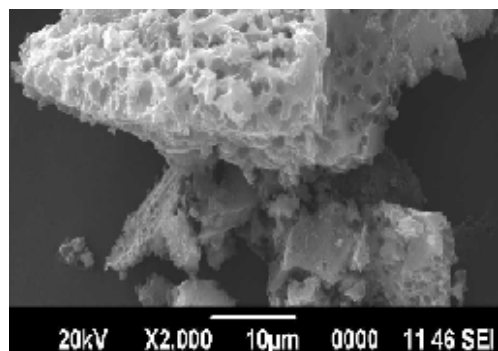


Fig. 1C SEM photograph of TP3 (2000 X)

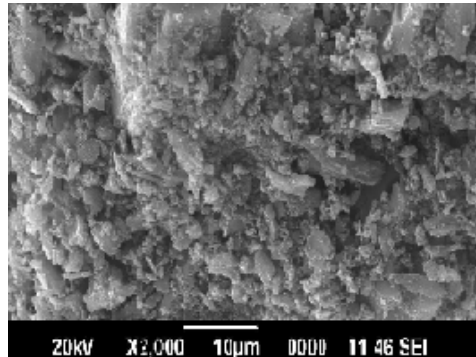


Fig. 1D SEM photograph of TP4 (2000 X)

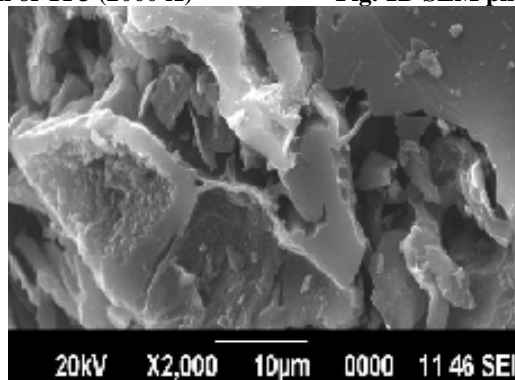


Fig. 1E SEM photograph of TP5 (2000 X)

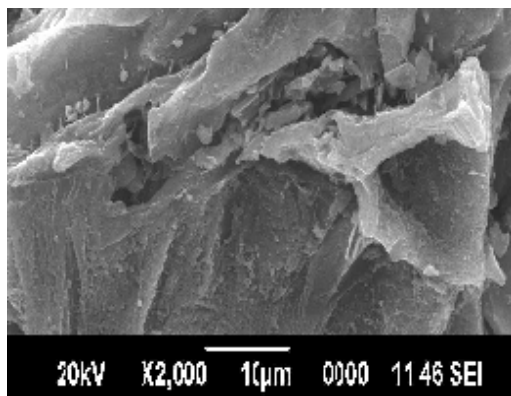


Fig. 1F SEM photograph of TP6 (2000 X)

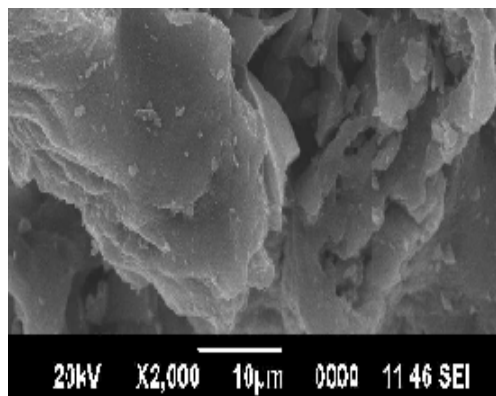


Fig. 1G SEM photograph of TP7 (2000 X)

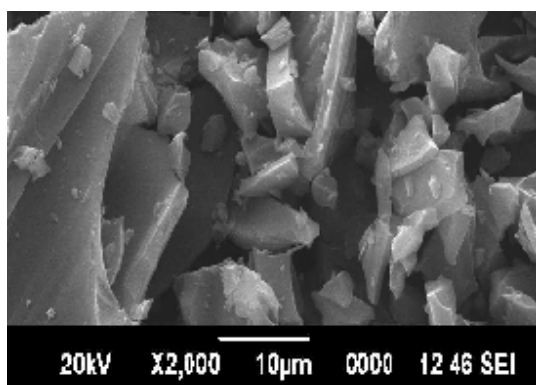


Fig. 1H SEM photograph of TP8 (2000 X)

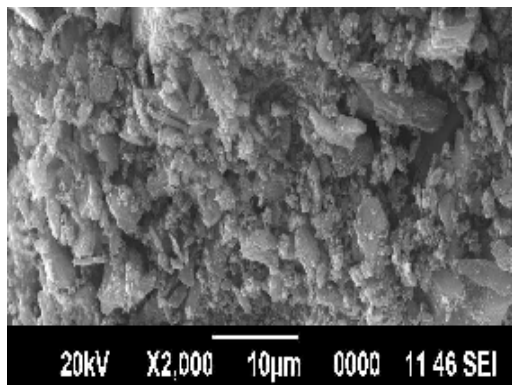


Fig. 1I SEM photograph of TP9 (2000 X)

3.3 Dye adsorption Characteristics

In this study Basic Green 4, Acid violet 49, Reactive Orange 4 and Direct Blue 71 were selected for the analysis of adsorption characteristics of TP3 at room temperature. The amount of Basic Green 4 adsorption is very high. All the anionic dyes (acid, direct, reactive dyes) show comparatively lesser adsorption than cationic dye Basic Green 4. Amount of Acid Blue 49 adsorption is slightly higher than Reactive Orange 4 and Direct Blue 71. This may be due to its smaller molecular size. Reactive Orange 4 and Direct Blue 71 are high molecular weight dyes; hence, they occupy more area in the activated carbon.

CONCLUSION

From the results of the present investigation,

1. A novel activated carbon can be conveniently and economically prepared from *Thevetia peruviana*.
2. By comparing the characteristics of activated carbon prepared by different methods the phosphoric acid impregnated carbon is assumed as a better activated carbon.
3. Porosity plays a major role in the selected adsorbent-adsorbate system.
4. KOH and H_3PO_4 activation process produces highly active carbon with high porosity.
5. Basic dye is absorbed more than the other dyes by the activated carbon obtained from H_3PO_4 activation process.

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