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PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBON FROM *EUPHORBIA TIRUCALLI L* WOOD FOR THE REMOVAL OF TEXTILE DYES FROM WASTE WATER

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ABSTRACT

In the present work, renewable lignocellulosic material *Euphorbia Tirucalli L* wood was used as a precursor for the production of activated carbon. The preparation includes both physical and chemical activation, which resulted in a porous structure and opening of pores on the surface of all activated carbon. Different activated carbons were prepared by pyrolysis, treatment using H_2SO_4, H_3PO_4, KOH and $ZnCl_2$ solutions, respectively. The activated carbon was characterized by pH, ash content, volatile matter, porosity, conductivity, bulk density, specific gravity, iodine number and adsorption of methylene blue. From the physico-chemical characteristic studies, the activated carbon prepared by impregnating the precursor with 35% H_3PO_4 solution followed by carbonization and activation at 800^oC was selected as better adsorbent due to its high surface area and high adsorption capacity. This carbon shows high adsorptive property for various dyes and could be used as a cost effective alternative novel adsorbent in waste water treatment for the removal of dyes.

Key words: *Euphorbia Tirucalli L* wood, Carbonization process, Activation, Characterization.

INTRODUCTION

Textile industries discharge huge amounts of polluted effluents into nearby water bodies. Most of the dyes used in textile industries are non-biodegradable due to their complex structures. The removal of dyes from industrial waste water before they are discharged into the water bodies is very important from health and hygiene point of view and environmental protection[1]. The improper disposal of dyes in waste water constitutes an environmental problem and can cause damage to the ecosystem[2]. Conventional biological processes are relatively inefficient for dye removal[3]. The waste water is usually treated with

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either physical or chemical processes like adsorption, coagulation, precipitation, filtration and oxidation. However, these processes are very expensive and cannot be effectively used to treat the wide range of dye waste[4].

Adsorption, an alternative technology for conventional waste water treatment has received considerable attention for the development of an efficient, clean and cheap technology. Activated carbon has been widely used as an adsorbent because of their extended surface area, microporus structure, high adsorption capacity and high degree of surface reactivity. But the cost associated with commercial adsorbents make this adsorption operation very expensive. Hence, there is a need for low cost and naturally available adsorbents, which can be used for the treatment of waste water contaminated with dyes. Natural materials, which are available in abundance or certain waste products from agricultural operations are used as inexpensive adsorbent and it also make them good source of raw material for activated carbons. The production of activated carbon from different materials like agricultural solid wastes saw dust[5], coconut husk[6], waste materials such as coir pith[7], eucalyptus bark[8], cassava peels[9], jackfruit peel[10], fly ash[11], pine saw dust[12] etc have studied.

The general process to produce activated carbon is based on carbonizing and activating the original carbonaceous material. Activation may achieved either physically or chemically[13]. The physical method consists of the pyrolysis of the precursor material and gasification of the resulting char in steam or CO_2. The formation of porous structure is achieved by the elimination of a large amount of internal carbon mass. Chemical activation involves impregnation of the raw material with chemical reagent such as H_3PO_4, KOH and $ZnCl_2$[14-16]. Major advantages of chemical activation compared with the physical activation are lower treatment temperatures and shorter treatment times. Activated carbon prepared by chemical method exhibits a larger surface area and better developed mesoporosity than physical activation. The type of precursor and the method employed for activation are the key factors that determine the quality of the carbon produced.

In this work, *Euphorbia Tirucalli L* wood, which is available in abundance, and renewable, is used for the production of activated carbon. *Euphorbia Tirucalli L* wood was carbonized by various physical and chemical methods.

EXPERIMENTAL

Euphorbia Tirucalli L wood was used as raw material for the preparation of activated carbon. The raw wood is cut into pieces and dried in sunlight for several days.

Then it can be used for the preparation of activated carbon. The physical and chemical characteristics of activated carbon were analysed and used for dye adsorption studies.

Carbonisation procedures[17]

Direct pyrolysis

The dried precursor material was carbonized at 400^{o}C and powdered well and then activated at 800^{o}C for 10 min. Finally, the carbon produced was washed with plenty of water repeatedly.

Carbonization with H_2SO_4

The dried material was treated with excess conc. H_2SO_4. Charring occurred along with evolution of heat. The mixture was left in air oven at 140 -160^{o}C for a period of 24 hours. Then the product was washed with plenty of water, dried at 110^{o}C and activated at 800^{o}C for 10 min.

Carbonization with H_3PO_4

The dried material was impregnated with 35% boiling solution of H_3PO_4 for 2 hours and left for 24 hours, then excess solution was decanted off and air dried. The dried material was carbonized at 550^{o}C for 1 ½ hrs in muffle furnace, powdered and activated at 800^{o}C for 10 min. The resulting carbon was washed with plenty of water to remove the acid, dried and powdered.

Carbonization with KOH

The dried material was soaked in 10% KOH solution and kept for 24 hours. At the end of this period, the excess solution was decanted off and air dried. Then the dried material was carbonized at 400^{o}C for 30 min., powdered well and activated in muffle furnace for 10 min. After the activation, the carbon was washed with 4N HCl to remove the cations. Then it was washed with plenty of water to remove the acid, dried and powdered.

Carbonization with $ZnCl_2$

The dried material was impregnated with 10% boiling solution of $ZnCl_2$ for 2 hours and left for 24 hours. Then excess solution was decanted off and air dried. The dried material was carbonized at 400^{o}C for 30 min. in muffle furnace, powdered and activated at 800^{o}C for 10 min. After the activation, the carbon was washed with 4N HCl to remove the cations. Then it was washed with plenty of water to remove the acid, dried and powdered.

Characterization studies

Physico-chemical characteristics of the activated carbon were studied as per the standard testing methods[18]. The N_2 adsorption-desorption isotherms of activated carbon were measured at 77K using N_2 gas sorption analyzer (Nova 1000, Quanta Chrome Corporation) in order to determine the surface area using the BET equation. The morphological characteristics of the samples were studied using Scanning Electron Microscope (make JEOL, Model 6390LA).

RESULTS AND DISCUSSION

General properties

The characteristics of the activated carbons prepared from *Euphorbia Tirucalli* L wood in various methods are presented in Table 1.

Table 1: List of activated carbon prepared from *Euphorbia Tirucalli L* and their preparation methods

Activated carbon	Preparation method
ET1	Pyrolysis process
ET2	H_2SO_4 process
ET3	H_3PO_4 impregnation
ET4	KOH impregnation
ET5	$ZnCl_2$ impregnation

The pH of activated carbon can be defined as the pH of a suspension of carbon in distilled water. The presence of acid functional groups such as carboxyl, phenolic and others on the surface of carbon may cause the acidic property of activated carbon. The pH of carbon prepared by acid processes (ET2, ET3 and ET4) were acidic. This may be due to the incorporation of acid group in the carbon structure[19]. The other remaining carbons ET1 and ET5 were basic in nature.

ET1, ET2, ET4 and ET5 showed higher conductivity and for ET3, it was moderate which may be due to the development of exchangeable sites on the surface of activated carbon [20]. The moisture content of the carbon has no effect on its adsorptive power and the carbon derived from KOH activation has high moisture contents of 10.8%.

The ash content of an activated carbon is the residue that remains when the carbonaceous portion is burned off. It depends on the type of raw material used for the preparation of activated carbon. High ash content is undesirable for activated carbon since it reduces the mechanical strength of carbon and affects adsorptive capacity. High ash content ultimately reduces the fixed carbon percentage. ET4 and ET5 have more ash contents, which may be incorporated by the activating agents.

Table 2: Physico-chemical characteristics of *Euphorbia Tirucalli L* activated carbon

Properties, carbon	ET1	ET2	ET3	ET4	ET5
pH	7.31	6.3	6.48	8.55	6.2
Conductivity, ms/cm	0.215	0.272	0.187	0.382	0.310
Moisture content %	8.2	9.4	10.4	10.8	10.3
Ash, %	9.2	10.4	10.8	12.3	15.2
Volatile matter, %	23.8	21.2	22.2	24.8	25.2
Bulk density, g/mL	0.56	0.51	0.56	0.54	0.53
Specific gravity	1.05	0.98	1.18	1.02	1.08
Porosity, %	46.61	47.95	52.54	47.06	50.9
Surface area (BET), m^2/g	329.05	390.32	857.85	504.47	561.31
Matter soluble in water, %	0.28	0.34	0.30	0.62	0.40
Matter soluble in 0.25 M HCl, %	1.82	1.30	1.28	1.36	1.48
Iodine number, mg/g	123	225	932	375	551
Methylene blue value mg/g	123	165	405	235	285
Fixed carbon %	58.8	59	56.6	52.1	49.3
Yield %	56.6	53	55.5	50.8	52.3

Naturally occurring plants have more volatile organic compounds and high percentage of volatile matter. High value of volatile matter reduces the quantity of fixed carbon. Due to high volatile matter, the percentage of fixed carbon was found low in ET5.

The apparent or bulk density is a measure of the weight of material that can be contained in a given volume under specified conditions. Higher density provides greater volume activity and normally indicates better quality activated carbon. Bulk density of all activated carbon do not show much variations indicating that it depends on the nature of the precursor and effect of activating agent is less.

Solubility studies of carbon in water and acid were performed to evaluate the amount of impurities present in carbon prepared by different carbonization process. The presence of impurities in carbon may affect the expected quality of the treated water during treatment. All carbon exhibits moderate level of impurities. The acid soluble matter was found to be low in the carbon prepared by acid processes.

Adsorptive properties are directly related to the porosity of activated carbon, as the highly porous carbon can adsorb large amount of organic compounds. ET3 is one of the porous carbons, whose porosity can be explained by iodine number and methylene blue value.

Iodine number is the most fundamental parameter used to characterize activated carbon performance. Iodine adsorption is a simple and fast adsorption method to determine the adsorptive capacity of activated carbon. Many carbons preferentially adsorb small molecules. It is a measure of the micropore content or pore volume available for the activated carbon by the adsorption of iodine from solution. Iodine number of commercial activated carbon ranges from 300 to 1200 mg/gm[21]. Iodine number of ET3 carbon is 932, which is comparable with the commercial carbon.

Some adsorbents have a mesopore structure, which adsorbs medium size molecules like dyes. Methylene blue has been used to determine the surface area pore size distribution of activated carbon. The methylene blue value represent the adsorptive capacity of activated carbon for molecules with dimensions similar to methylene blue and to the surface area, which results from the presence of pore sizes greater than 1.5 nm. ET3, ET4 and ET5 carbons showed methylene blue value greater than 200 indicates that the carbons are good for dye adsorption.

Higher yields are desirable in activated carbon production and it helps to reduce production costs. High yield was obtained in the KOH process followed by H_3PO_4 impregnation process. Optimum volatile matter and ash content give higher percentage of fixed carbon. Based on this characterization studies, it can be concluded that *Euphorbia Tirucalli* L wood is a good precursor for the production of activated carbon with high efficiency. ET3 posses high surface area and porosity and it has been selected as the best carbon for the further dye removal studies.

Scanning electron microscope analysis

Analysis of SEM graphs of activated carbon are presented in Fig. 1 to 5 and showed pores and rough surfaces on carbon sample,which indicated that porous network. ET3 with

2000X magnification showed the morphology of highly porous activated carbon.

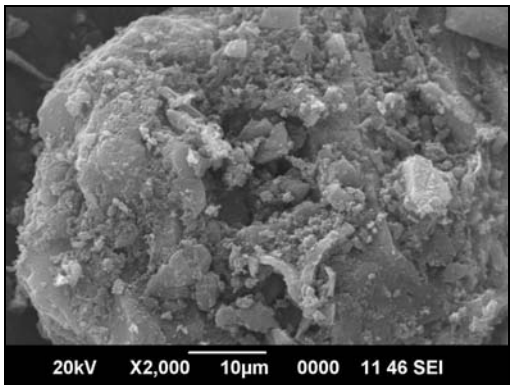

Fig. 1: SEM photograph of ET1

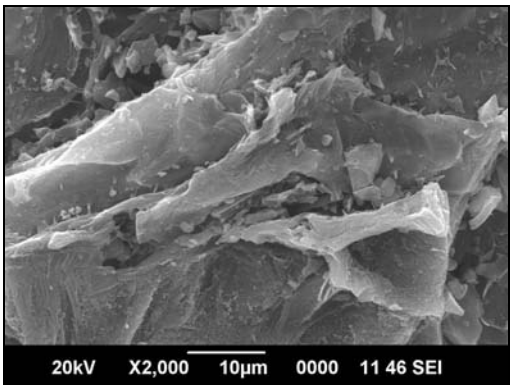

Fig. 2: SEM photograph of ET2

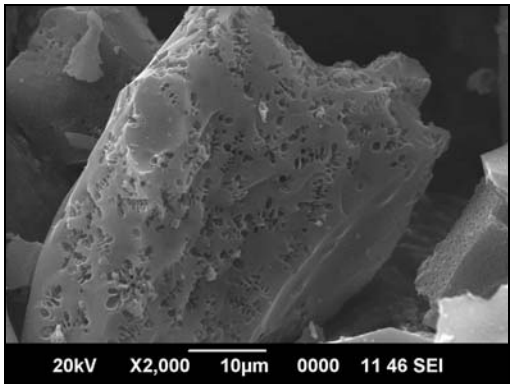

Fig. 3: SEM photograph of ET3

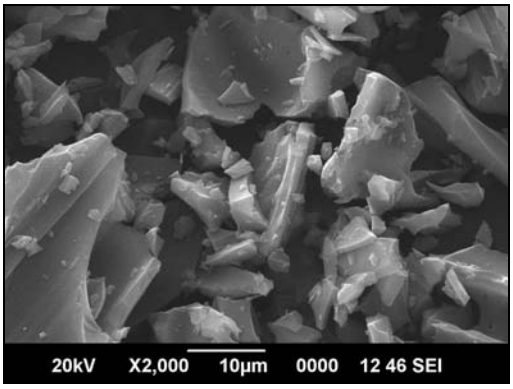

Fig. 4: SEM photograph ET4

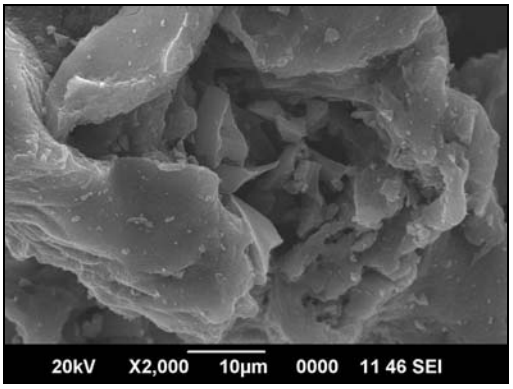

Fig. 5: SEM photograph of ET5

The adsorption studies were carried out for four categories of dyes-acid (Acid Orange 10), basic (Basic violet 3), reactive (Reactive red) and direct (Direct blue) using activated carbon and compared. Figures 6 to 9 show the structure of selected dyes and Figure 10 shows the percentage of various dyes adsorbed onto various activated carbons from *Euphorbia Tirucalli* L wood.

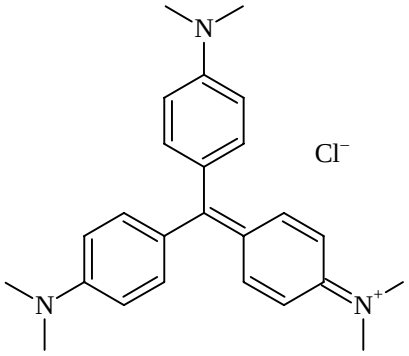

Fig. 6: Basic violet 3

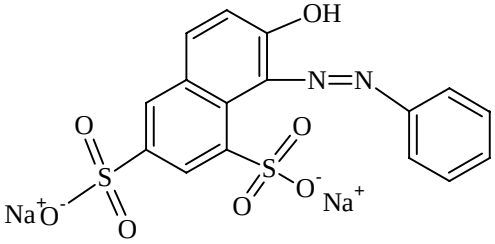

Fig. 7: Acid orange 10

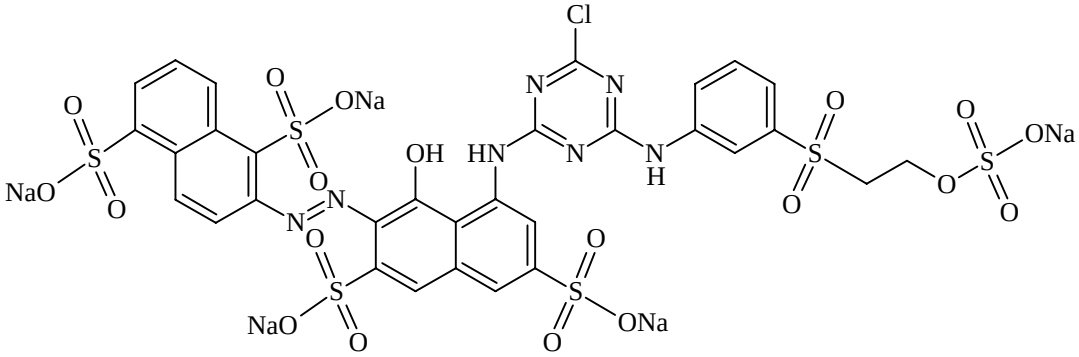

Fig. 8: Reactive red

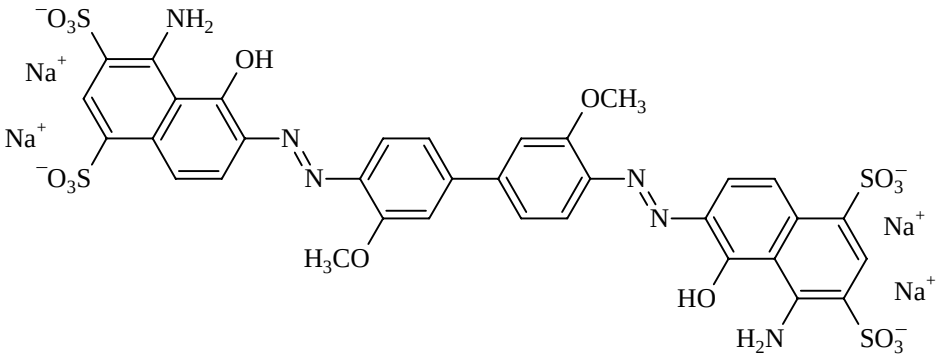

Fig. 9: Direct blue

ET3 carbon shows an excellent adsorption for basic dyes as compared to other anionic dyes. Due to its smaller molecular size, the percentage of acid orange10 adsorbed is slightly higher than other anionic dyes by all the carbons. Reactive and direct dyes are high molecular weight dyes and occupy more area in activated carbon and shows lower adsorption. ET3, ET2 and ET5 carbons show good performance for dye adsorption of all categories of dyes.

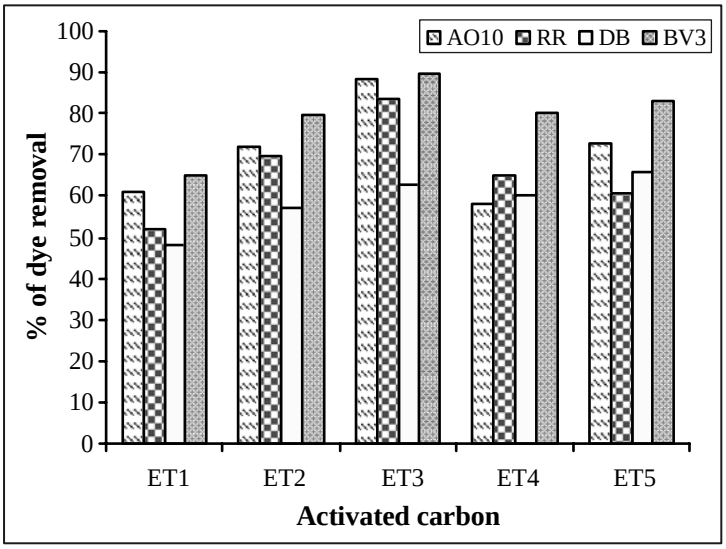

Fig. 10: Percentage of various dyes adsorbed onto various activated carbon from *Euphorbia Tirucalli* L wood

CONCLUSIONS

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

(i) *Euphorbia Tirucalli* L wood has been conveniently utilized to prepare the activated carbon.

(ii) Activated carbon prepared by various methods can be assessed as a better carbon, which can be explained by its characterization studies.

(iii) Activated carbons with high surface area are prepared by H_3PO_4 and $ZnCl_2$ impregnation followed by activation process.

(iv) Porosity explained by iodine number and methylene blue value plays a vital role in carbon-dye adsorption system.

(v) The adsorption capacities of various carbons for different categories of dyes are tested.

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