

Physico-chemical and adsorption studies of activated carbon from Agricultural wastes

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ABSTRACT

*It has been widely recognized that dye removal by activated carbon adsorption is due to the surface action between the dye and the functional groups present in the surface of the carbon. An effective usage of the adsorbent necessitates a deeper understanding of the adsorption characteristics. The present study examined the use of modified activated carbon derived from the seeds of widely available plant source of *Martynia annua* L and *Xanthium strumarium*. A series of activated carbon samples were prepared by subjecting the materials to various chemical processes. The physico-chemical properties and sorption abilities were compared. Adsorption of commercially used dye materials of various concentrations were studied with prepared activated carbon samples from batch tests. These materials accrue superior properties and good adsorption behaviors. The adsorption capacities of four of the selected derived carbon samples were much greater than the capacities of the other carbon. The results reveal that the prepared activated carbon could be employed as a low cost alternative for decolorizing the coloring agents from waste water and industrial effluents.*

Key Words: Activated carbon, Surface area, Adsorption, Surface chemical groups.

INTRODUCTION

A dye can generally be described as a colored substance that has an affinity to the substrate to which it is being applied and is used to impart color to materials of which it becomes an integral part. Many industries such as dyestuff's, paper, textile and plastics use dyes in order to color their products and also consume substantial amount of water [1]. Synthetic dyes and pigments are extensively used in dyeing and printing industry. Over ten thousand tons per year and approximately 10000 dyes are produced annually worldwide, of which 10 % is lost in the industrial effluents [2]. The presence of very small amounts of dyes in water even less than 1ppm for some dyes is highly visible and undesirable [3]. The removal of color from textile waste water is a major environmental problem and they are the first contaminant to be recognized in water [4]. Colored water is also objectionable on aesthetic grounds for drinking and agricultural purposes [5]. As synthetic dyes in wastewater cannot be efficiently decolorized by traditional methods, the adsorption of synthetic dyes on inexpensive and efficient solid supports was considered as a simple and economical method for their removal from water and wastewater. Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal and synthetic resins. Carbons with excellent surface properties and specific functionalities should be developed to create a high affinity for adsorbate adsorption.

Activated carbon has been extensively used for the purpose of water purification. In particular, it has been commonly used for the removal of organic dyes from textile waste water. In order to improve the adsorption capability of the raw carbon, it is subjected to various suitable chemical treatments. Carbon based sorbents show excellent adsorption properties for a considerable number of synthetic dyes. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available control technologies [6]. However, the preparation of carbon sorbents is generally energy consuming. Consequently, the commercially available products are fairly expensive. Since, a large amount of carbon sorbent is needed for the removal of dyes from a large volume of effluent, the expenses involved hamper their application [7]. The use of carbon based on relatively expensive starting materials is also unjustified for most pollution control applications [8]. Hence, widely available plant sources are utilized to deduce the concentration of dyes from wastewater and industrial effluents. The physico-chemical and adsorption characteristics of activated carbon derived from *Martynia annua L* and *Xanthium strumarium* have been measured and their capacity to remove commonly used synthetic dyes such as Direct Congo Red, Basic Methylene Blue, Reactive Blue MR and Acid Blue has been evaluated.

MATERIALS AND METHODS

The raw seeds of *Martynia annua L* and *Xanthium strumarium* were collected from in and around Erode Taluk, Tamil Nadu, India. They were broken in to small pieces, dried in sunlight until the moisture was evaporated. The dried materials were used for the preparation of activated carbons using physical and chemical activation methods as stated below.

2.1 Carbonization Procedures [9]

2.1.1 Acid processes

The dried materials is treated with excess of Sulphuric acid and Hydrochloric acid. Charring of the materials occurred immediately with evolution of fumes and heats in both the cases. After the reaction subsided, the materials were left in air oven at 140-160°C for a period of 24 hours. The dried masses were washed with excess of water to remove the free acid residues. They were dried at 110 °C, sieved and finally activated at 800 °C.

The material was soaked with 10% Phosphoric acid for a period of 24 hours. After impregnation, the excess acid was decanted. The treated mass was subjected to carbonization at 400 °C and powdered well. It was washed with excess of water to confiscate excess acids present. The material was sieved and subjected for activation at 800 °C for a period of 10 minutes.

2.1.2 Carbonization with Sulphate and chloride salts

The materials to be carbonized were soaked with 10% solutions of Na₂SO₄ and ZnCl₂ salt solutions for a period of 24 hours. After impregnation the liquid portions decanted off and dried at 120 °C. The dried and neutralized mass was subjected to carbonization process at 400 °C, powdered well and thermally activated at 800 °C for a period of 10 minutes [10].

2.1.3 Carbonization with Base

The dried raw materials permeated with the 10% KOH solution for 24 hours and dried well for over 12 hours in air oven at 120°C. They were washed with excess of water and the dried mass was subjected to carbonization process at 400 °C, powdered well and thermally activated at 800 °C for a period of 10 minutes.

The powdered materials are sieved to get the particle size in 180 to 300 μm. Materials treated with Conc. H₂SO₄, Conc.HCl, 10% H₃PO₄, 10%KOH, 10% ZnCl₂ and 10% Na₂SO₄ which are named as M1, M2, M3, M4, M5, M6 and X1, X2, X3, X4, X5, X6 respectively. The physico-chemical properties of treated activated carbon were measured by suitable standard methods [11]. The pH and conductivity were analyzed using Elico make pH meter (LI-120) and conductivity meter (M-180) respectively. Moisture Content (%) by mass, Ash Content (%) by mass, Bulk Density (g/L), Specific gravity, Water soluble matter, Acid soluble matter, Iodine number (mg/g), Surface Area (m²/g), Phenol adsorption capacity were analyzed as per standard procedures[12]. The Zero point charge of the carbon were measured by using the pH drift method [13]. The decolorizing power of the different activated carbons were carried out using Basic Methylene Blue dye solution of known concentration dispersed with known quantity of activated carbon and stirred for a pre-determined duration as per the standard techniques [14].

2.1.4 Batch adsorption studies

Different concentrations of individual dye solutions such as Direct Congo Red, Basic Methylene Blue, Reactive Blue MR and Acid Blue were prepared with distilled water. The concentrations of dyes in solutions were determined before and after adsorption using Perkin-Elmer UV-visible spectrophotometer. The amount of dye adsorbed and adsorption efficiency was calculated as follows:

$$\text{Efficiency (\%)} = ((C_0 - C) / C_0) \times 100$$

Where,

C_0 = initial dye concentration (mg/l),

C = residual dye concentration (mg/l),

RESULTS AND DISCUSSION**3.1 Physico-chemical characteristics**

Physico-chemical parameters of activated carbon obtained from *Martynia annua L* and *Xanthiyam strumarium* were illustrated in table 1 and 2 respectively. The pH of the carbon derived from acid treatment was slightly lower than the carbon impregnated with KOH and other salts. The results reveal that the acid treated carbon samples have effectively adsorbed the basic dye. Conductivity values indicated in tables 1 and 2 shows that the carbon samples were almost free from dissolved impurities. It has been found that the pores of the carbon were completely available for the accumulation of adsorbate [15, 16 & 17]. Low moisture content of carbon indicates that the carbon samples have poor affinity on water. Eventhough moisture content of the carbon doesn't affect the adsorptive power, it dilutes the carbon which demands the use of additional weight of carbon during treatment processes [15].

Table 1. Physico-Chemical parameters of Activated Carbon from *Martynia annua L*

Parameters	M1	M2	M3	M4	M5	M6
pH	6.93	6.24	6.13	7.65	7.25	7.32
Conductivity, mS/cm	0.18	0.19	0.22	0.41	0.44	0.35
Moisture Content, %	3.18	4.12	3.34	3.86	4.23	3.12
Ash Content, %	17.5	4.7	4.1	2.7	9.3	13.9
Bulk Density, g/L	0.77	0.78	0.73	0.58	0.79	0.48
Specific Gravity	0.83	0.89	1.66	0.61	0.63	0.56
Water Soluble Matter, %	0.88	0.56	0.80	1.98	2.13	3.31
Acid Soluble Matter, %	0.49	1.23	0.86	1.12	0.96	0.87
Zero Point Charge in pH Units	7.5	7.3	7.1	7.4	7.2	8.0
Iodine Number, mg/g	871	642	906	438	642	1024
Surface Area, m ² /g	882	688	1028	532	786	1142
Phenol Adsorption Capacity, mg/g	5.83	4.21	6.43	4.68	5.17	6.64
Decolorizing Power, mg/g	26	18	32	16	18	38

Ash content level of carbon derived from *Xanthiyam strumarium* were higher than the carbon prepared from *Martynia annua L*. The ash content of the samples substantiate that *Xanthiyam strumarium* have higher inorganic constituent than *Martynia annua L*. The carbon having little amount of ash content may remove the inorganic contaminants effectively [15 & 18]. Higher bulk densities of the carbon from *Xanthiyam strumarium* are suitable for treatment processes, as the low density carbon suspends on water and the treatment processes cannot be effective. Also the lower bulk density values illustrate that the carbon samples are highly branched and porous with more void space [19]. Carbon prepared from the treatments with KOH, ZnCl₂ and Na₂SO₄ gives higher water soluble constituents, which implies that the presence of water soluble impurities may have impact on the treated water. The values of water soluble matter and acid soluble matter are low in carbon prepared from acid treatment. This depicts that the acid treatment lowers the leachable constituents. According to Boehm, only strong acidic carboxylic groups are neutralized by weak bases like sodium carbonate. Strong bases like NaOH reacted with weakly acidic phenolic groups. The zero point charge value of H₃PO₄ treated carbon X3 indicates the presence of acidic oxygen functional groups in its surface [20].

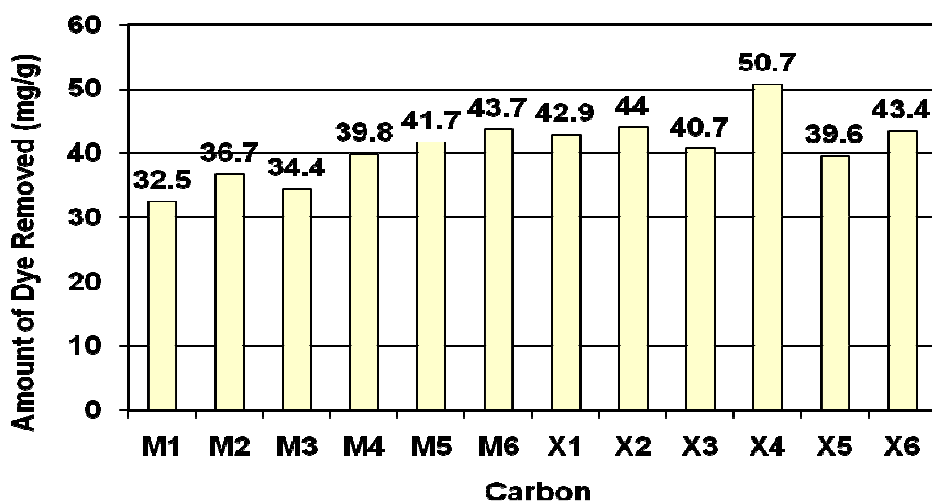
Table 2. Physico-Chemical parameters of Activated Carbon from *Xanthiyam strumarium*

Parameters	X1	X2	X3	X4	X5	X6
Ph	6.25	6.36	7.05	7.67	7.44	7.57
Conductivity, mS/cm	0.23	0.27	0.24	0.4	0.49	0.46
Moisture Content, %	3.39	3.29	4.12	3.14	4.24	4.13
Ash Content, %	18.84	5.12	6.23	14.27	11.02	4.19
Bulk Density, g/L	0.88	0.91	0.86	0.63	0.85	0.73
Specific Gravity	0.91	1.85	0.97	0.73	0.62	1.38
Water Soluble Matter, %	0.96	0.86	0.67	2.37	2.26	1.04
Acid Soluble Matter, %	0.55	0.92	1.36	0.93	1.34	1.18
Zero Point Charge in pH Units	8.2	7.6	6.2	7.8	7.3	7.9
Iodine Number, mg/g	899	984	670	1052	802	511
Surface Area, m ² /g	901	1056	717	1136	815	561
Phenol Adsorption Capacity, mg/g	5.98	6.48	4.56	6.53	5.32	4.76
Decolorizing Power, mg/g	29	35	25	43	24	21

The zero point charge implies that the prepared carbon is free from surface charges nearby neutral pH. Hence the carbon samples are suitable for the treatment of water even at the neutral medium. The higher level of iodine number reveals that the presence of high porosity in the carbon. These results are supported by the surface area, phenol adsorption capacity and decolorizing power values of the carbon samples. Chemically modified carbon was found to be an excellent adsorbent for the basic, acidic and dispersed dyes but direct dye showed less affinity for adsorption [21]. The usefulness of carbon is a result of their specific surface area. Carbon X4 and X2 removes effectively the Direct Congo Red dye from its aqueous solution.

The efficiency of removal of Direct Congo Red dye by various carbon samples is

X4 > X2 > M6 > X6 > X1 >> M5 > X3 > M4 > X5 > M2 > M3 > M1.

**Figure1. Removal of Direct Congo Red dye by prepared activated carbon samples**

Carbon X4 and X2 having higher surface area, removes the Direct Congo Red dye from aqueous solutions effectively (Fig. 1). This carbon samples also has the easily exchangeable chloride radicals on its surface. Carbon M3 having higher surface area but with bulky phosphate radicals may decrease the adsorptive efficiency. The similar results were also reported by the removal of Direct Congo Red dye by waste red mud [22] a by-product of aluminium production with 90-min of equilibrium time, rice hull ash [23] and banana pith [24]. The adsorption of

dyes is higher on activated carbon having higher value of surface area. The presences of surface polar groups on the adsorbent have greater influence on the adsorptive nature of the carbon [25].

The efficiency of removal of Basic Methylene Blue dye from aqueous solution by various carbon samples (Fig. 2) is $M3 > X3=X4 > M5 > M6 > M2=X6 > X2 > X5 > X1 > M4 > M1$.

Carbon M3 and X3 has greater adsorption due to the presence of acidic functional groups in it. The higher surface area of the KOH treated carbon X4 may be the reason for its affinity towards the adsorption of basic dye compared with carbon M4 which has lower surface area. The similar adsorptive results of basic dyes, Basic Methylene Blue and Gentian Violet by carbonaceous material produced from coffee grounds depended upon the acidic polar groups on the adsorbent material [21] also reported. Each low-cost adsorbent has its specific advantage in waste water treatment. For example clay minerals exhibit a strong affinity for basic dye [26].

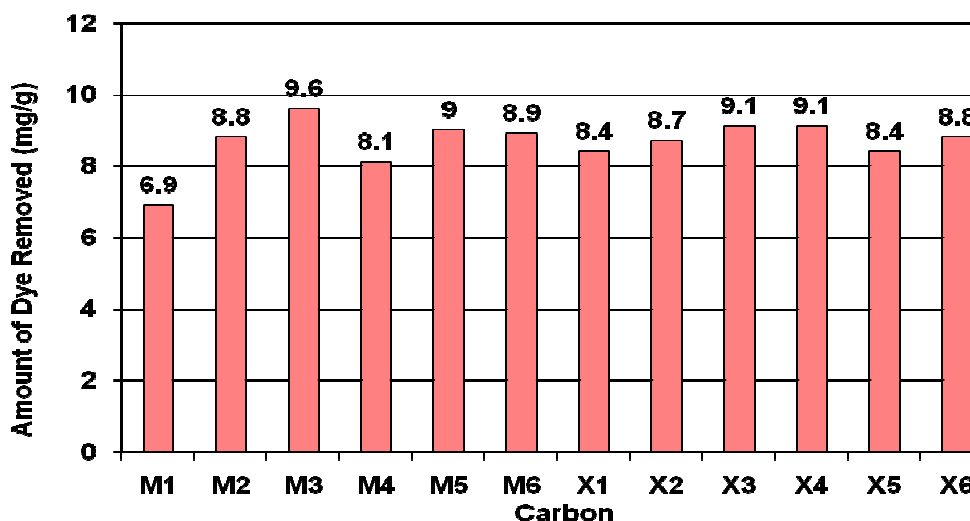


Figure 2. Removal of Basic Methylene Blue dye by prepared activated carbon samples

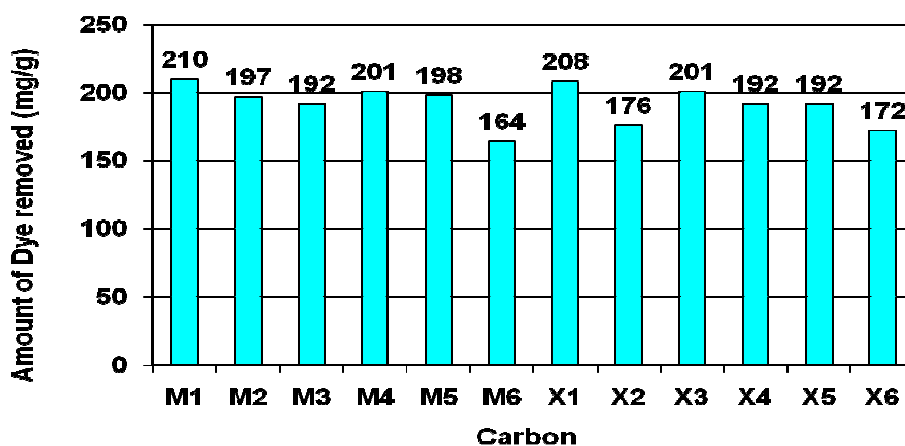


Figure 3. Removal of Reactive Blue MR dye by prepared activated carbon samples

The carbon M1 and X1 shows greater amount of adsorption of Reactive Blue MR dye (Fig. 3). The order of removal of Reactive Blue MR dye by the carbon samples is $M1 > X1 > M4=X3 > M5 > M2 > X4=X5 > M3 > X2 > X6 > M6$.

Carbon M1 and X1 have greater affinity towards the removal of anionic Reactive Blue MR dye. This is due to the presence of acidic functional groups in their voids. Similar investigations reported the effect of modified carbon surface in adsorption of three anionic reactive dyes remazol yellow, remazol black and remazol red from its aqueous solutions [27]. The recent reported adsorption capacity values (q_m) 712.3, 278, 714 of Reactive red2 [28], Reactive red5 and Reactive orange107 [29] respectively with commercially activated carbon materials and Adsorption of Reactive red120, Reactive red141 and Reactive red2 [30] with low cost adsorbent yields the q_m values 48.31, 56.18, 62.5 respectively indicates the substantial removal of reactive dye with chemically modified surfaced carbon.

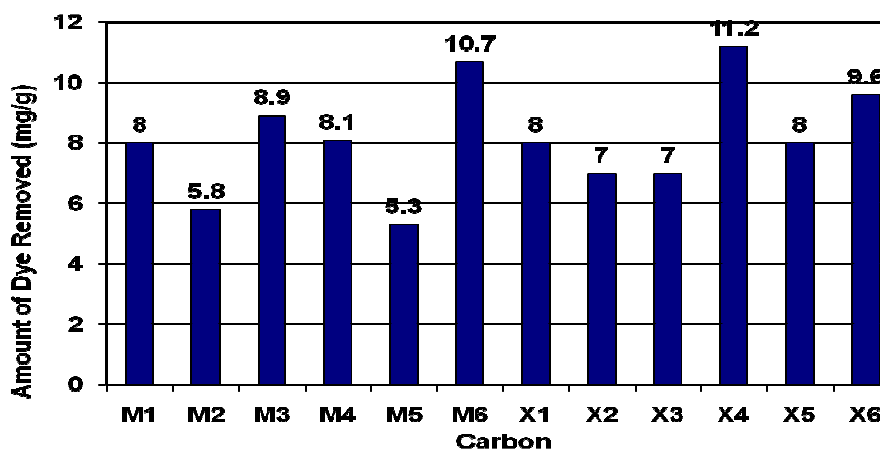


Figure 4. Removal of Acid Blue dye by prepared activated carbon samples

The carbon M6 and X4 shows the greater removal of acid blue dye (Fig. 4) due to their higher surface area. This is also supported by their iodine number, phenol adsorption capacity and decolorizing power values. The efficiency of removal of Acid Blue dye from its aqueous solution by treated carbon is $X4 > M6 > X6 > M3 > M1 > M4 = X1 > X2 = X3 > M2 > M5$.

Adsorption of acid dye by base treated carbon X4 having higher surface area reveals the presence of anionic surface groups in its surface. This is supported by its pH value. Due to the lack of greater surface area and lower iodine number of same KOH treated carbon M4 shows lower adsorption capacity towards the adsorption of Acid Blue dye. Adsorption of acid dyes like Acid orange7 by prokaryotic organism gram negative bacteria *Aeromonas hydrophilla* [31], *Burkholderia capacia* [32], *Sphingomonas Xenophaga* [33] and gram positive bacteria like *Caulobacter subribrioides* [34] are highly selective in nature but the removal process was reported to be slow. By the use of activated carbon, other components of the waste water also be adsorbed by the carbon and the competition among the adsorbate can influence the dye binding capacity of supports in an unpredictable manner. Moreover, when compared with other treated activated carbon samples, M1, M3, X3 and X4 carbon show maximum adsorption property.

3.2 Scanning Electron Micrograph studies

The morphology of the prepared activated carbon samples surface was examined using Scanning Electron Micrographs. These micrographs (Fig. 5) give an appreciation of the porosity of an adsorbents and hence a qualitative assessment of their ability to adsorb the dye molecules in solution. M3, X3 and X4 have many pores in a honeycomb shape were clearly found on the surface. This shows that H_3PO_4 and $ZnCl_2$ were effective to create well-developed pores with uniform distribution on the surface of the precursor, hence leading to the activated carbon with large surface area and porous structure.

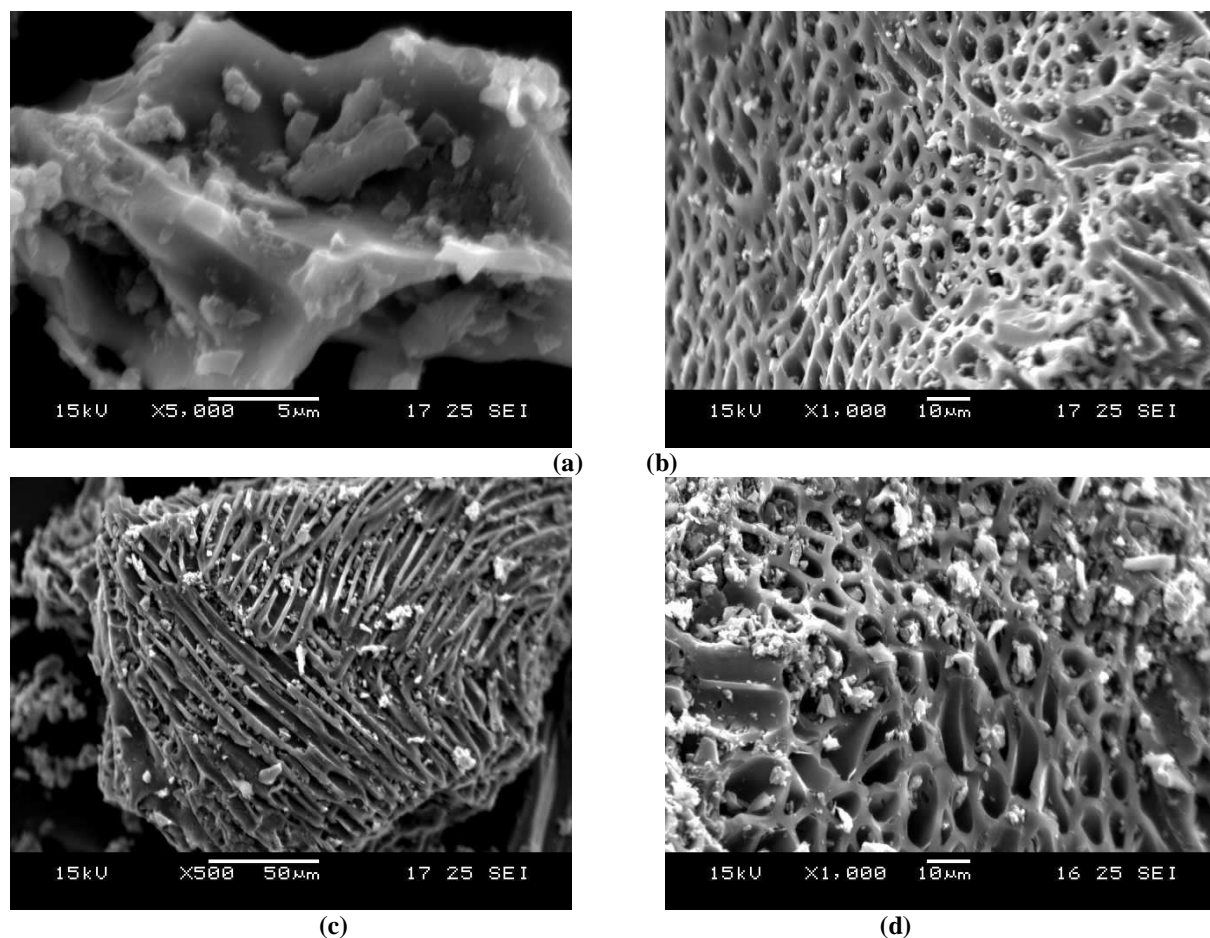


Figure 5. SEM image of Activated Carbon

- (a) M1- H_2SO_4 treated activated carbon (5000X) (b) M3- H_3PO_4 treated activated carbon (1000 X)
 (c) X3- H_3PO_4 treated activated carbon (500X) (d) X4- $ZnCl_2$ treated activated carbon (1000X)

CONCLUSION

From the results of the present investigation reveals that an activated carbon can be prepared conveniently and economically from plants sources. The prepared adsorbents have a substantial variation in the dye removal capacity. These carbon samples significantly remove the dyes from aqueous solutions based on their physico-chemical properties. The characterization studies are very useful to find the superior grade carbon for adsorption processes. Activated carbon with good surface properties from various treatment procedures were identified, their surface chemical groups can play a key role in removing variety of dyes from its aqueous solutions.

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