Removal of Toxic Dyes from Textile Effluents by Using Activated Carbons from Jackfruit Waste

T. V. Nagalakshmi*[1], K. A. Emmanuel[2]

[1]*Department of chemistry, Laki Reddy Bali Reddy College of Engineering, Mylavaram -A.P., (India)*

[2]*Department of Chemistry, Sir C.R.Reddy Autonomous College, Eluru A.P., (India)*

ABSTRACT

Water is the most precious, limited natural resource on this biosphere which is essential to the survival of all living beings. Discharge of effluents from industrial processes adds hazardous chemicals to surface and ground water. In the present study activated carbons were prepared from Jack fruit waste and named as JC_{600}, JC_{KOH} and JC_{HNO3}.These activated carbons were characterized by using different analytical techniques. The pore structures of the resulting carbon were analyzed using N_2 adsorption, X-ray diffraction (XRD) and scanning electron microscope (SEM). Thermal stability of carbon was analyzed by thermogravimetric analysis (TGA) temperature programmed desorption (TPD) studies. The nature of functional groups present on surface of activated carbons was analyzed by FTIR techniques. Finally the JC_{600}, JC_{KOH} and JC_{HNO_3} used in decolorization of carcinogenic textile dyes from textile effluents collected from textile industry located in Chittoor district, A.P., India by adsorption technique and observe the chemical kinetics involved in the adsorption of textile dyes.

Key words: - **Jack fruit waste, TGA, TPD, FTIR, textile dyes**

I. INTRODUCTION

Textile industries consume large volumes of water, dyes and auxiliary chemicals for processing of textiles. Due to incomplete exhaustion and washing operations, 10-20% of dyes were discharged into effluents [1]. Many of these dyes were toxic and carcinogenic thus affecting the aquatic biota and human health [2]. The world population was expected to be increased by 35% by 2050 [3]. This population growth will increase the production of clothes, which in turn, increases fresh water use. So conserving water and reducing water pollution will become a challenging and essential task for textile industries.

1.1Material and Methods

1.2.1 Preparation of activated carbon

Jack fruit waste was collected from state horticulture mission, Paderu, Visakhapatnam, A.P., India. The rind and pulp waste of fruit was used as precursor for preparation of activated carbon. The waste was washed with hot distilled water to remove dirt and dehydrated at $105^{o}C$ until constant weight was obtained. This dried waste was then cut into small pieces impregnated with K_2CO_3 solution. This mixture was dehydrated in an oven overnight at $105^{o}C$. The impregnated precursor was carbonized in uniform nitrogen flow to $600^{o}C$. The heating was provided at rate of $10^{o}C$ min^{-1}. The prepared activated carbon was cooled to room temperature and washed with hot distilled water to remove remaining chemical and filtered. The washing and filtration steps were repeated until the filtrate showed neutral pH. The activated carbon was sieved to 45 mesh and was named in accordance with its activation temperature as JC_{600}.

In order to introduce different functional groups, JC_{600} was divided into two parts. One part was subjected to liquid phase oxidation with 0.2N HNO_3 and the other part was soaked in 0.2N KOH for 3 hr and evaporated at $110^{o}C$. Both carbons were washed with distilled water until filtrate showed neutral pH. These carbons were dehydrated in an oven overnight at $105^{o}C$ and named as 'JC_{HNO_3}' and 'JC_{KOH}', indicating the chemical activating agent.

2.2.2 Characterization of prepared activated carbons:

The pore structures of the resulting carbons were analyzed using N_2 adsorption, X-ray diffraction (XRD) and scanning electron microscope (SEM). Thermal stability of carbons was analyzed by thermogravimetric analysis (TGA) temperature programmed desorption (TPD) studies. The nature of functional groups present on surface of activated carbons was analyzed by FTIR techniques.

2.2.3 SEM analysis:

A scanning electron microscope SEM Hitachi- S520 (OXFORD LINK-ISIS) was used to study the texture of the surface of activated carbons.

2.2.4 FTIR analysis:

The surface chemistry characterization of each activated carbon was performed by Fourier Transform Infrared Spectroscopy (FTIR) to identify its surface functional groups. FTIR spectra were recorded on Thermo Nicolet Nexus 670 spectrometer in the wave number range 400-4000 cm^{-1}. To prepare pellets, samples were first ground to powder in an agate mortar and then mixed with KBr at a mass ratio of 1:500. A hydraulic press was used to press the resulting mixtures to discs of 10 mm in diameter at 10 MPa for 5 min.

2.2.5 TPD analysis:

TPD analysis was performed on MICROMERITICS CHEMISORB 2750 instrument. Activated carbon samples were kept in high pure Helium flow for 10 min. Gas changed to 10% NH_3 in Helium at a rate of 30 ml min^{-1} flow. NH_3 adsorbed for 30 min. Gas changed to pure Helium (30 ml min^{-1}) and physisorbed ammonia was removed for stable baseline status.

2.2.6 TGA analysis:

The thermo gravimetric analysis (TGA) experiments were performed on a SDT Q 600 TGA analyzer (TA instrument). Each time, activated carbon sample was heated from room temperature to $900^{o}C$ under nitrogen atmosphere at a heating rate of $10^{o}C$ min^{-1}.
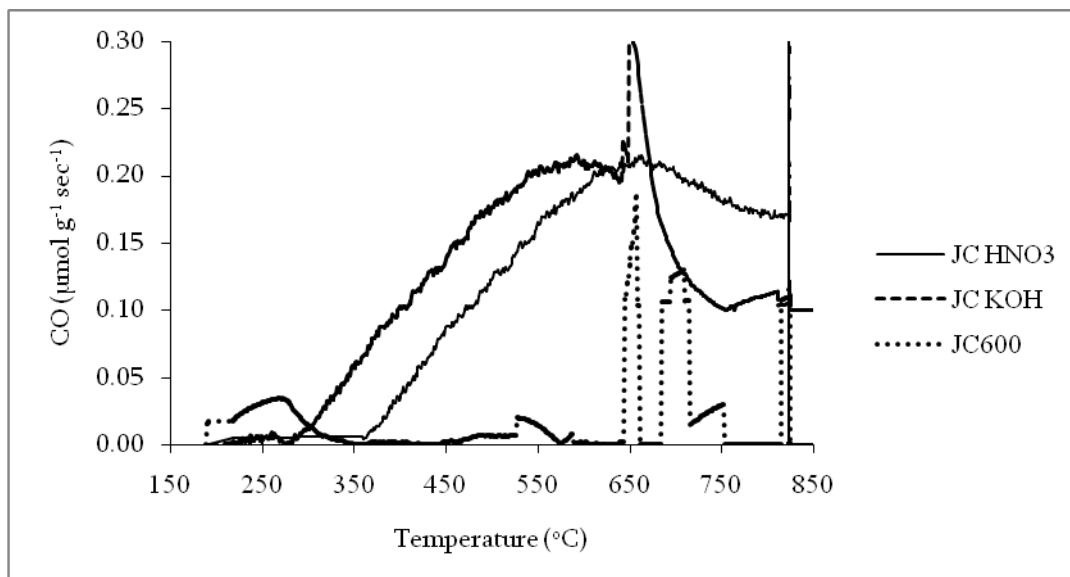
2.2.7 XRD analysis:

Powder X-ray diffraction patterns were recorded on a Philips: PW1830 at 30 kV and 15mA (Cu Kα radiation) at a step size of 0.01^{0} and at a wavelength 0.154 nm.

Table.1 XRD parameters of JC_{600}, JC_{HNO_3} and JC_{KOH}

Sample	d_{002} (nm)	L_c (nm)	L_a (nm)
JC_{600}	0.315	1.83	2.23
JC_{HNO_3}	0.324	1.99	2.18
JC_{KOH}	0.314	1.97	2.38

2.1 (a)

2.1 (b)

International Journal of Advance Research in Science and Engineering
Volume No.06, Special Issue No.(01), December 2017
www.ijarse.com

IJARSE
ISSN: 2319-8354
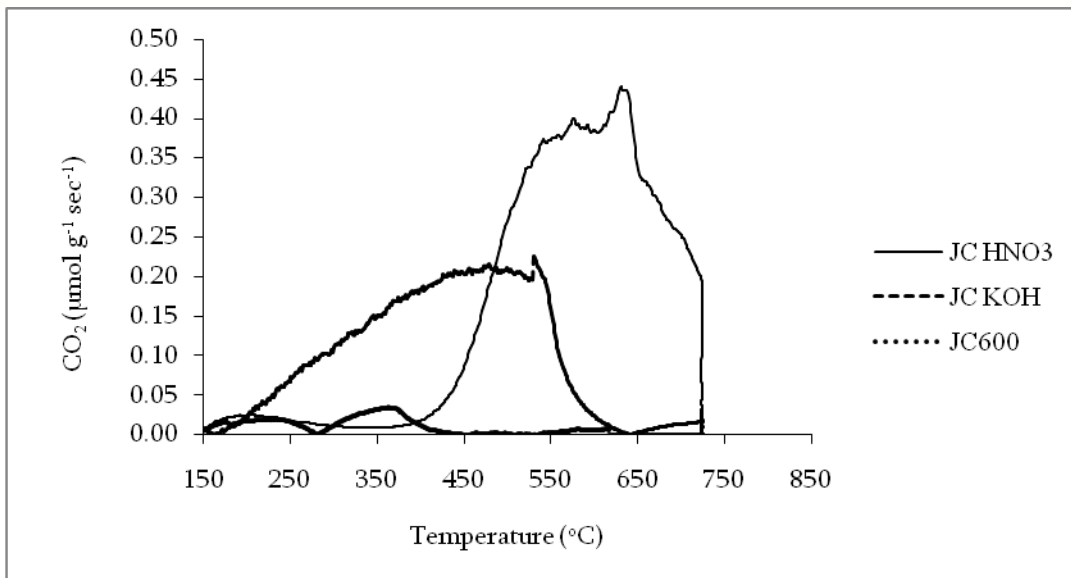
Figure 2.1(a). CO_2 evolution profiles of JC_{600}, JC_{HNO_3} and JC_{KOH}

Figure 2.1(b). CO evolution profiles of JC_{600}, JC_{HNO_3} and JC_{KOH}
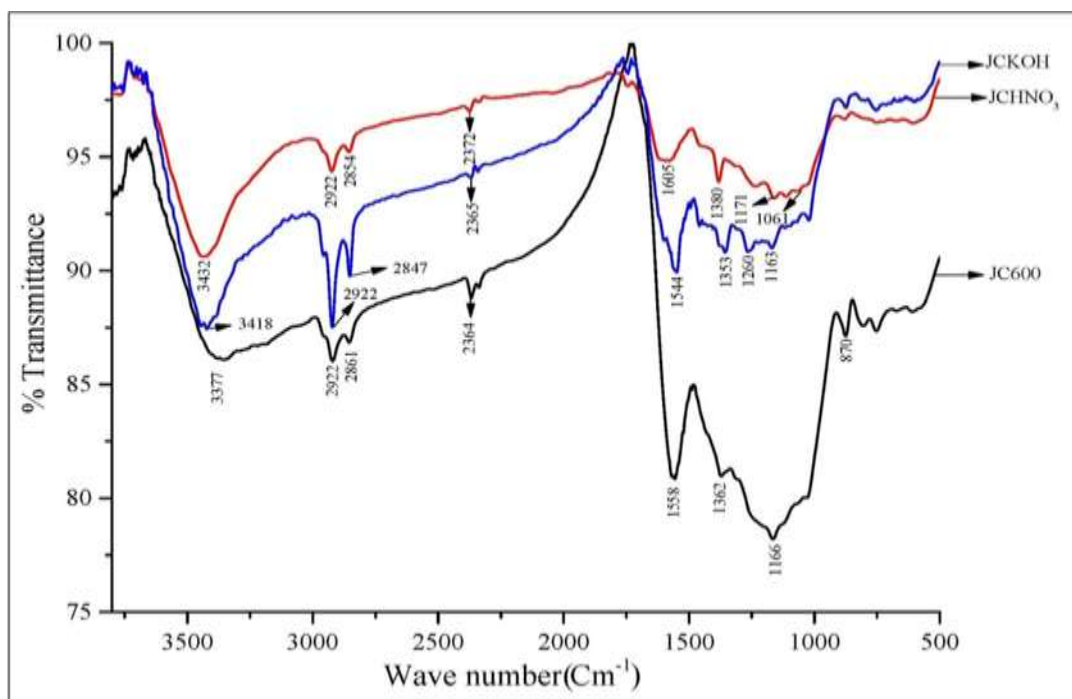
Figure 2.2. FTIR analyses of JC_{600}, JC_{HNO_3} and JC_{KOH}

2.3(a)
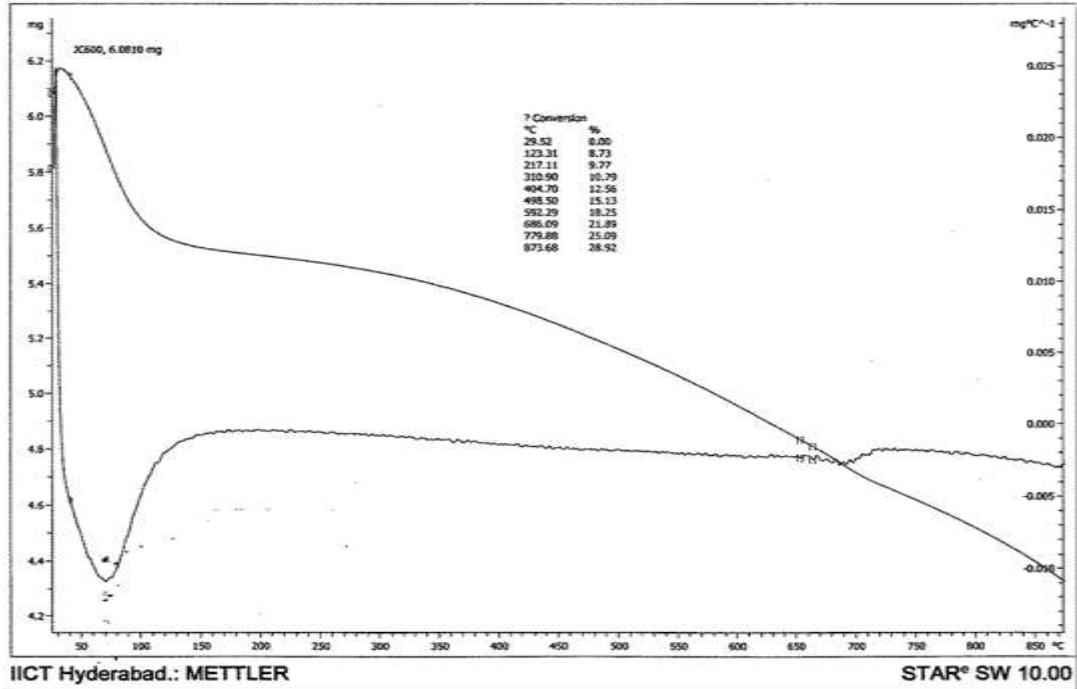
Figure 2.6(a) .TGA of JC$_{600}$

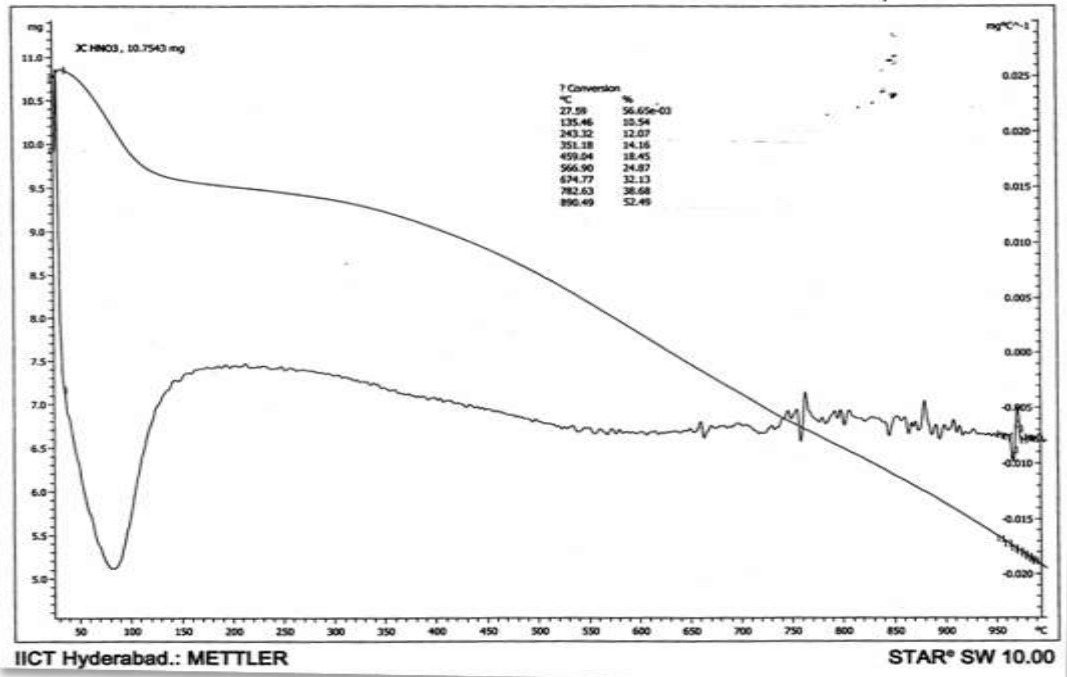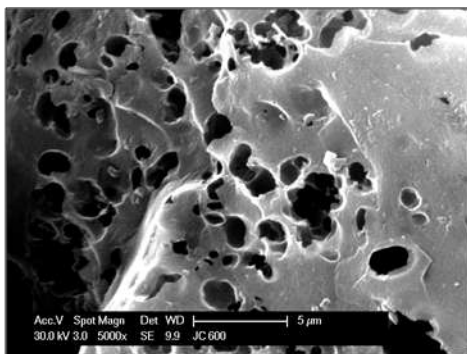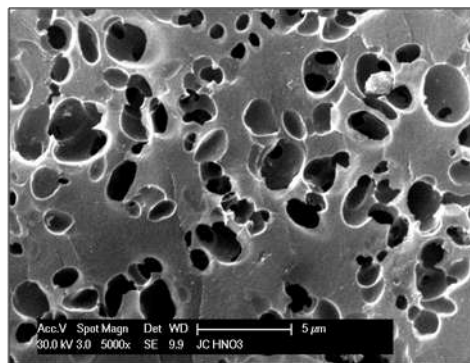2.3(b)
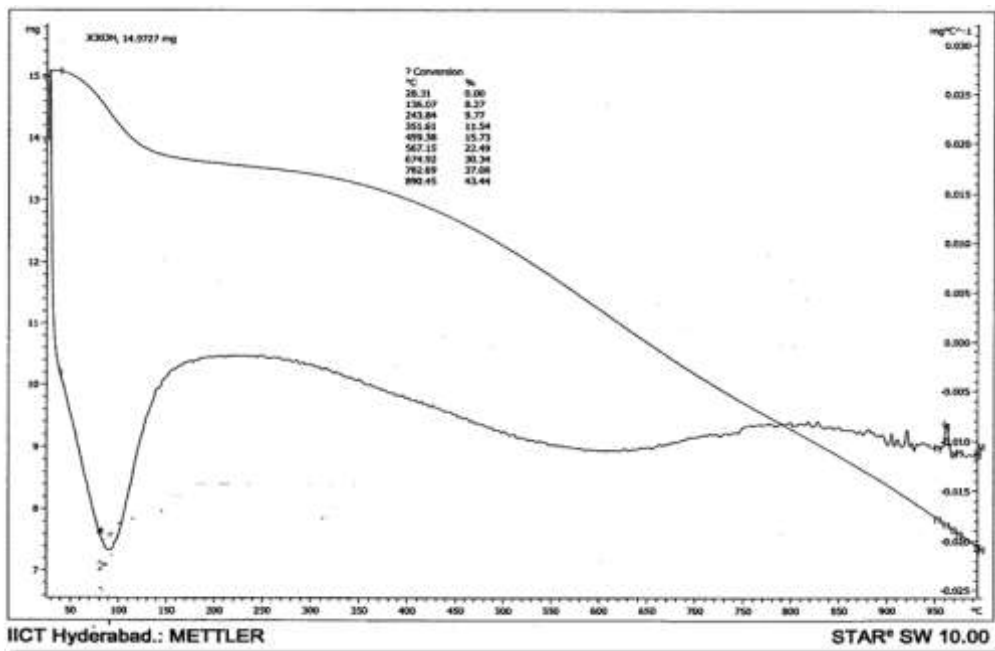
2.3(c)

Figure 2.3(b). TGA of JC$_{HNO_3}$

Figure 2.3(c). TGA of JC$_{KOH}$

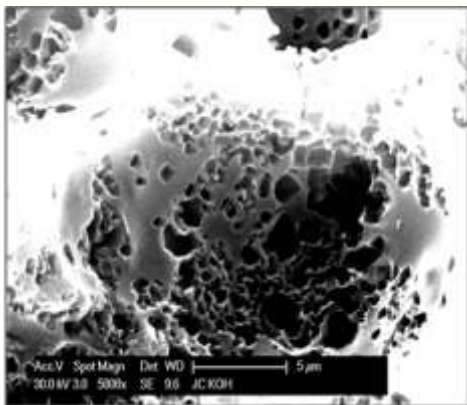2.4(a)   2.4(b)

2.4(c)

Figure 2.4. SEM images of (a) JC_{600}, (b) JC_{HNO_3} and (c) JC_{KOH} at 5 k X magnification
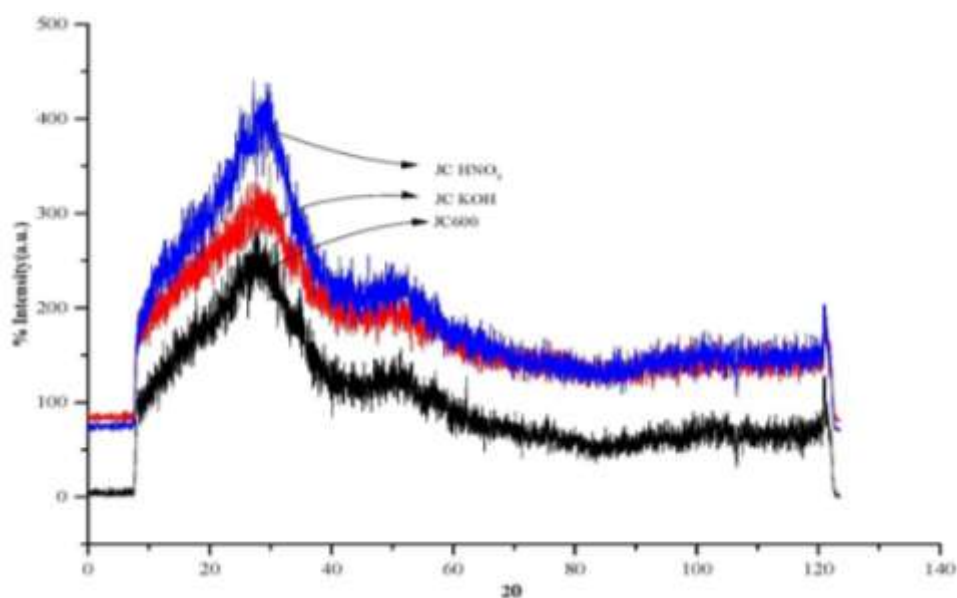

Figure 2.5. XRD graph of JC_{600}, JC_{HNO_3} and JC_{KOH}

III.RESULTS AND DISCUSSIONS

Jackfruit waste contains natural polymers like cellulose, lignin and hemicelluloses [4]. During carbonization process these polymeric structures decompose and liberate hydrogen, oxygen, nitrogen and other elements in the form of tar and gases. The presence of K_2CO_3 in the interior of Jackfruit waste might have restricted the formation of tar by forming cross-links and inhibited the shrinkage of precursor material by occupying certain substantial volumes [5]. K_2CO_3 will be reduced in inert atmosphere by carbon to give elemental potassium and carbon monoxide [6, 7, 8].

$$K_2CO_3 + 2C \rightarrow 2K + 3CO \ \ldots\ldots\ldots\ (1)$$
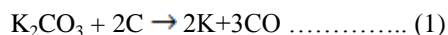
Hence potassium will be intercalated between the graphite layers or from graphite-potassium intercalation compounds [9]. The presence of intercalated potassium inhibited the shrinkage of carbon during activation process at elevated temperatures. In hot distilled water washing process of prepared activated carbon, potassium was removed and left micropores. As a result the surface area of impregnated activated carbons was also increased when compared with $JC_{Non-activated}$.

2.3.1 TPD analysis:

Fig.2.1 (a) and 2.1(b) shows TPD analysis profile for CO_2&CO desorption from JC_{600}, JC_{HNO_3} and JC_{KOH}. Surface oxygen groups present on these activated carbons decomposed upon heating. They release CO_2 and CO at different temperatures. CO_2 peaks result from the decomposition of carboxylic acids at low temperature or lactones at high temperature and anhydrides give both CO and CO_2. Groups like phenols, carbonyls, ethers and quinones originate CO peaks. When compared with JC_{HNO_3} (shown in Fig. 2.1(a)), JC_{KOH} had less number of oxygen functional groups, but much higher than JC_{600}. In both CO_2 and CO desorption profiles, JC_{600} showed less oxygen content. However, comparatively, JC_{600} showed more oxygen content in CO profile than that of CO_2 desorption studies. It may be assumed that during preparation of activated carbon, heat treatments under inert atmosphere at high temperature effectively removed oxygen. However active sites present on activated carbon might have re-adsorbed oxygen to less extent. Hence JC_{600} had very less oxygen content which in other words provide more hydrophobic surface. Activated carbon with more hydrophobic surface was one of the required properties for adsorption of non-ionic organic pollutants from aqueous solution. In desorption studies of CO profile, JC_{KOH} showed release of CO at around 750^oC. It evidenced that soaking the activated carbon in potassium hydroxide solution changed the surface chemistry of carbon by introducing different oxygen functional groups.

2.3.4 FTIR analysis:

If surface functional groups of carbon materials were modified then their practical usage will be extended to different adsorption applications [10, 11, 12]. It was identified that surface chemistry of carbon influence both electrostatic and non-electrostatic interaction and will work as vital factor for adsorption mechanism from aqueous solutions.

FTIR spectra contain peaks which are indicative of specific chemical bond. So it will give information about functional groups on surface of activated carbon. By considering depth of peak line and locations, the type of functional group can be qualitatively guessed. Since activated carbons were black materials that absorb almost all of the radiation in visible spectrum, and peaks obtained was usually a sum of interactions of different types of groups [13]. Hence information from different experimental techniques like TPD, XPS along with FTIR were used to identify functional groups present on activated carbon surfaces.

JC_{600} was prepared in inert atmosphere. According to Radovic *et al* [14] preparing activated carbon under inert atmosphere will produce activated carbon with less number of surface functional groups. Hence activated carbons produced in inert atmosphere possess high hydrophobicity due to the removal of hydrophilic surface functionalities, particularly various acidic groups [15,16,17].

FTIR spectra of JC_{600}, JC_{HNO_3} and JC_{KOH} were shown in Fig.2.2. A distinct peak was observed at 1558 cm^{-1} for JC_{600} only. This might be due to polyaromatic C=C stretching vibrations in sp^2-hybridized carbons [19, 20]. This indicated the non-polar (hydrophobic) nature of JC_{600}. However, C=O stretching vibrations of quinones might also be included at this peak. According to Jagtap *et al* [21], jack fruit waste had small quantity of phenolic and flavonoid compounds. These might have produced quinone type functional groups on surface of JC_{600}. Bands in the range 1350-1380 cm^{-1} were attributed to C-N bond stretching vibrations of aryl amines which might appear because jack fruit contains amino acids [22]. A series of small peaks in the region 870 cm^{-1} were attributed to aromatic C-Cl bonds.

In comparison with other FTIR graphs (of JC_{HNO_3} & JC_{600}), JC_{KOH} is having very sharp peaks at 2922 and 2841 cm^{-1}. This might be attributed due to the presence of 2H-chromene as reported elsewhere [23, 24]. The V-shaped band at 3424 cm^{-1} might be attributed to the O-H stretching of alcohols. JC_{KOH} activated carbon was prepared by treating JC_{600} with potassium hydroxide and evaporated at 110^oC and then washed with distilled water. It was observed that JC_{600} was having quinone type functional groups. Quinones were sensitive to the action of aqueous alkalis, in the presence of which, depending on the conditions, they decompose to organic acids [25] form hydroxy-derivatives of quinones [26] or polymerize to products of the type of the huminic acids [27]. The presence of 2H-chromene might be the result of these reactions. Similar type of surface modifications were observed when char of *Jatropha curcas L* waste was mixed with KOH solution and evaporated at 80^oC [28]. The bonds present at 870 cm^{-1} were disappeared in JC_{KOH} activated carbon. The C-Cl bond might have been converted to C-OH bond during the treatment of JC_{600} with KOH.

5 TGA analysis:

TGA plots of JC_{600}, JC_{HNO_3} and JC_{KOH} were shown in Fig.2.3. In all TGA plots before reaching 150^oC temperature, there was little fall (8-10%) in weight of each carbon. In this region moisture content of carbon samples was removed. From this temperature, there was a gradual decrease in weight of each carbon sample. However, at 890^oC, the fall is about 52% in JC_{HNO_3} and 43% in JC_{KOH}. It might be due to the difference in presence of surface oxygen functional groups in these two carbons. And these oxygen functional groups might have reacted with carbon to escape as CO_2 and CO gases. In JC_{600}, the fall is only 28% at this temperature. It could be due to the presence of less number of oxygen functional groups. This observation was also in good agreement with the FTIR analyses of corresponding activated carbons shown in Fig.2.2. However the loss in weight was small up to 300^oC for all carbons.

2.3.6 SEM analysis:

SEM images of JC_{600}, JC_{HNO_3} and JC_{KOH} carbons of K_2CO_3 impregnation were shown in Fig.2.4. Pore structure was not disturbed due to chemical activation with HNO_3 and KOH.

2.3.7 X-Ray diffraction:

The XRD pattern of JC_{600}, JC_{HNO_3} and JC_{KOH} was shown in Fig.2.5.

The values of d_{002}, L_c, and L_a of selected activated carbons were tabulated in Table 2.4. For these activated carbons, the diffraction profiles exhibited broad peaks at around 27 and 48° which were assigned to the reflection from (0 0 2) and (1 0 0) planes, respectively. The occurrence of broad peaks at 2θ indicated an increasing regularity of crystal structure and resulted in better layered alignment [29].

XRD graph pointed that JC_{600} was not structurally altered during liquid phase activation with HNO_3 and KOH. Nearly equal d_{002} values of all the three carbons indicated that no appreciable change had happened in JC_{600} while introducing different functional groups upon its surface. It may be due to the reason that liquid phase activation of activated carbon with dilute chemicals (0.2N HNO_3 or 0.2N KOH) does not change the absolute carbon porosity in a drastic way [30].

IV.APPLICATION

Textile effluents sewage directly enters water streams without any treatment. The color and the non-biodegradable nature of the spent dyebaths constitute serious environmental problems and various deleterious effects caused by them. The toxicity was not only caused by textile dyes but also by a large number of different textile chemicals. The effluents are collected from three different places of their disposal. The efficiency of prepared carbon adsorbents in decolorizing these textile effluents was studied.

Figure 3.1. (a) Commercial dyes & other chemicals for dyeing fabric (c) Washing dyed fabric (d) Effluent ready to discard (shown with arrow)

able .2. Testing the efficiency of prepared adsorbents in color removal from textile effluents

Samples	pH	COD (mg l⁻¹) JC_{600}	JC_{HNO3}	JC_{KOH}	BOD (mg l⁻¹) JC_{600}	JC_{HNO3}	JC_{KOH}	Color absorbance (absorbance m⁻¹) JC_{600}			JC_{HNO3}			JC_{KOH}			% Color removal		
								nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Sample 1	6.7	176	87	37	21	20	20	84	115	98	65	70	79	53	55	62	44.22	54.55	46.52
Sample 2	8.2	157	79	26	45	35	34	35	63	52	29	58	31	22	44	23	46.35	48.24	57.89
Sample 3	6.4	215	110	59	15	11	11	98	75	51	62	42	36	49	35	31	53.34	62.37	54.08

3.1. Decolorization of textile effluents with increasing adsorbent dosage:

To achieve better results like 7, 5 and 3 m⁻¹ absorbance at wavelengths of 436, 525 and 620 nm respectively, the dose of adsorbents increased for treatment of three effluents at same contact time of 60 min and obtained values were presented in Table 2 and the corresponding graphs were shown in Fig.3.2 for three samples. In all cases, it was observed that as the adsorbent dosage increased, the percent removal of color of the effluents also increased.
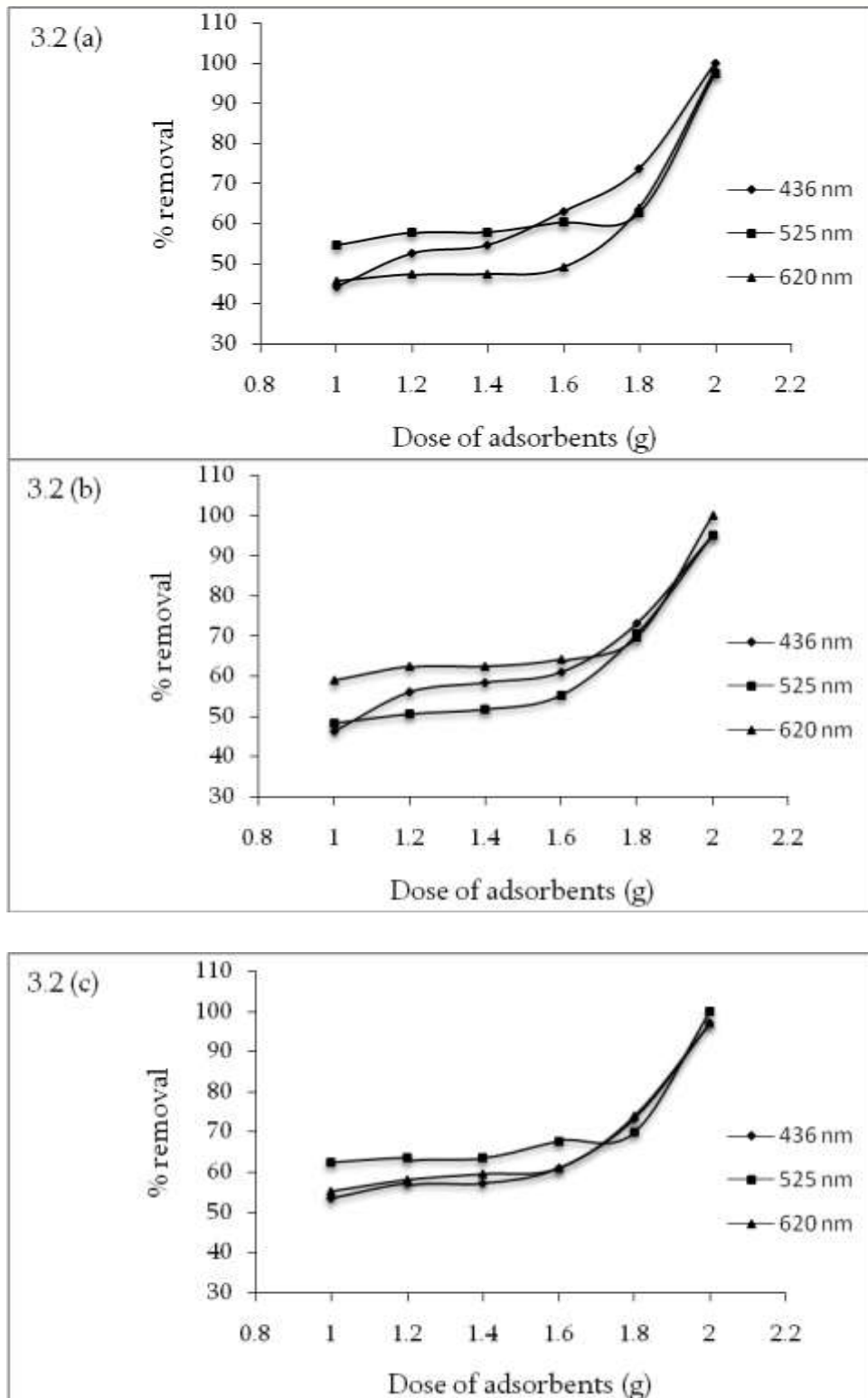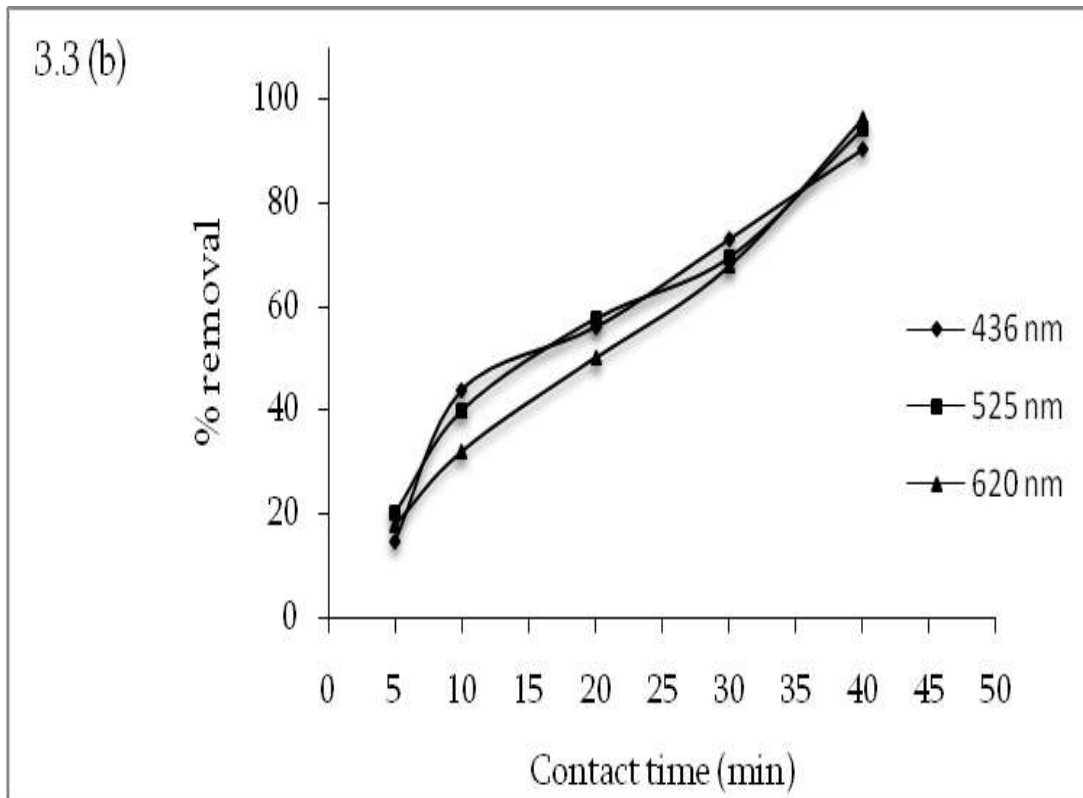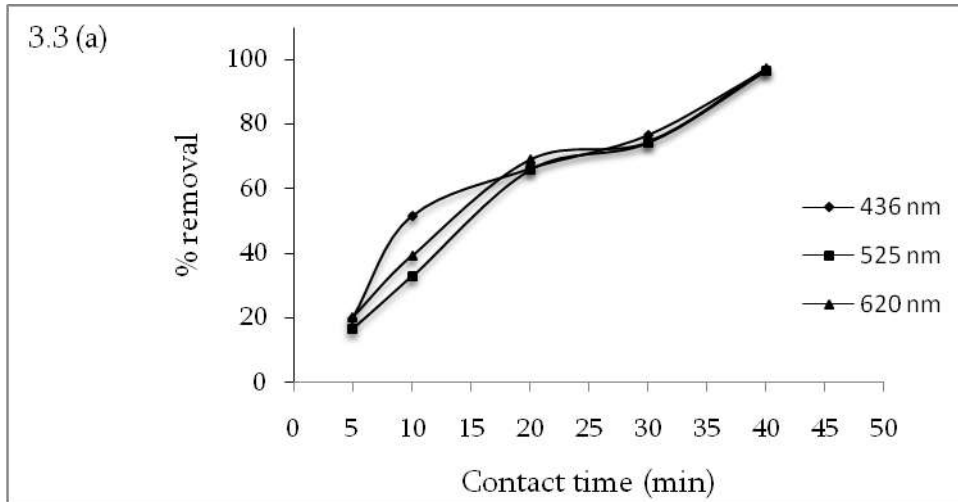
Figure 3.2(a). Effect of adsorbents dose in color removal from sample 1

Figure 3.2(b). Effect of adsorbents dose in color removal from sample 2

Figure 3.2(c). Effect of adsorbents dose in color removal from sample 3

3.2. Decolorization of textile effluents with increasing contact time:

To find the optimum contact time of adsorbents for removal of color from textile effluents to their permissible value, the same experiment was done by increasing the agitation time with fixed adsorbent dose (2 g). The observed values were tabulated in Table.2 and the corresponding graphs were shown in Fig.3.3 for three samples.
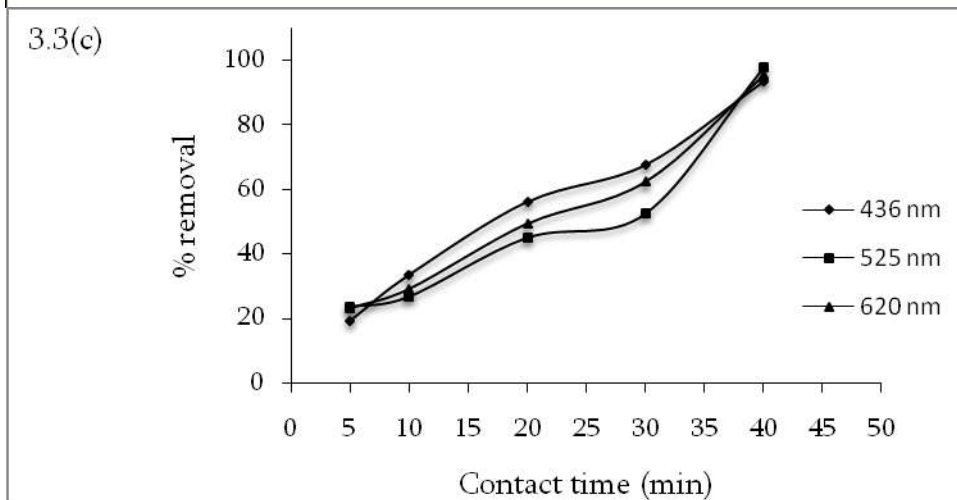
Figure 3.3(a). Effect of contact time of adsorbents in color removal from sample 1

Figure 3.3(b). Effect of contact time of adsorbents in color removal from sample 2

Figure 3.3(c). Effect of contact time of adsorbents in color removal from sample 3

It was noticed that in all adsorption systems the dye removal was increased with increase in agitation time and reached equilibrium within 40 min. The observed percent removal of sample1, 2, and 3 were 97.37, 96.43 and 95.66% respectively.

V. CONCLUSION

All the three activated carbons were thermally stable up to 300°C. Hence these can be used for adsorption of pollutants from aqueous solutions at elevated temperatures also. FTIR analysis pointed out that surface chemistry was peculiar and specific for each activated carbon. From XRD analysis report it can be concluded that the interlayer spacing of all activated carbons was nearly same. It was found that JC_{HNO_3} contained high percentage of carboxylic acids, JC_{KOH} was enriched with more number of hydroxyl functional groups and JC_{600} was having hydrophobic surface with less oxygen content. Hence these carbons can be used to adsorb different types of organic pollutants from water. The collected effluents were highly colored and prior treatment was always necessary before discharging. The prepared activated carbons successfully removed the color of the effluents. It was observed that besides removal of color, there was concurrent reduction of COD and BOD of the effluents. The effluents treated until the acceptable limit of 7, 5 and 3 m^{-1} absorbance reached at the standard wavelengths of 436, 525 and 620 nm respectively within 40 min and by using 2g of each adsorbent.

REFERENCES:

[1.]   Inbaraj, B.S. and Sulochana, N. 2002. Evaluation of a carbonaceous sorbent prepared from pearl millet husk for its removal of basic dyes. Journal of Scientific and Industrial Research. 61, 971-978.

[2.]   Kyzas, G.Z. and Kostoglou, M. 2014. Green adsorbents for wastewaters: a critical review. Materials. 7(1), 333-364.

[3.]   United Nations, Department of Economics & Social affairs (UN/DESA), 2012. World population prospects: the 2012 revision. Available http://esa.un.org/unpd/wpp/Publications/Files/WPP2012_HIGHLIGHTS.pdf

[4.]   Prahas, D., Kartika, Y., Indraswati, N. and Ismadji, S. 2008. Activated carbon from jackfruit peel waste by H_3PO_4 chemical activation: Pore structure and surface chemistry characterization. Chemical Engineering Journal. 140(1-3), 32-42.

[5.]   Adinata, D., Wan Daud, W.M.A. and Aroua, M.K. 2007. Preparation and characterization of activated carbon from palm shell by chemical activation with K_2CO_3. Bioresource Technology. 98(1), 145-149.

[6.]   McKee, D.W. 1983. Mechanisms of the alkali metal catalyzed gasification of carbon. Fuel. 62(2), 170-175.

[7.]   Hayashi, J., Horikawa, T., Takeda, I., Muroyama, K. and Ani, F.N. 2002. Preparing activated carbon from various nutshells by chemical activation with K_2CO_3. Carbon. 40(13), 2381-2386.

[8.]   Okada, K., Yamamoto, N., Kameshima, Y. and Yasumori, A. 2003. Porous properties of activated carbons from waste newspaper prepared by chemical and physical activation. J. Colloid Interface Sci. 262(1), 179- 193.

[9.]   Xiang, X., Liu, E., Li, L., Yang, Y., Shen, H., Huang, Z. and Tian, Y. 2011. Activated carbon prepared from polyaniline base by K_2CO_3 activation for application in supercapacitor electrodes. Journal of Solid State Electrochemistry. 15(3), 579-585.

[10.] Izquierdo, M.T, Rubio, B., Mayoral. C. and Andres, J.M. 2001. Modifications to the surface chemistry of low-rank coal-based carbon catalysts to improve flue gas nitric oxide removal. Applied Catalysis B: Environmental. 33(4), 315-324.

[11.] Shim, J.W., Park, S.J. and Ryu, S.K. 2001. Effect of Modification with HNO_3 and NaOH on Metal Adsorption by Pitch-based Activated Carbon Fibers. Carbon. 39(11), 1635-1642.

[12.] Yin, C.Y., Aroua, M.K. and Daud, W.M.A.W. 2007. Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions. Separation and Purification Technology. 52(3), 403-415.

[13.] Zawadzki, J. 1988. Infrared spectroscopy in surface chemistry of carbons in chemistry and physics of carbon. Thrower. P.A. (Ed.), Marcel Dekker, New York, 21, 147-386.

[14.] Radovic, L.R., Silva, I.F., Ume, J.I., Menendez, J.A., Leony Leon, C.A. and Scaroni, A.W. 1997. An experimental and theoretical study of the adsorption of aromatics possessing electron-withdrawing and electron-donating functional groups by chemically modified activated carbons. Carbon. 35(9), 1339-1348.

[15.] Menendez, J.A., Illan-Gomez, M.J., Leony Leon, C.A. and Radovic, L.R. 1995. On the difference between the isoelectric point and the point of zero charge of carbons. Carbon. 33(11), 1655-1657.

[16.] Menendez, J.A, Phillips, J., Xia, B. and Radovic, L.R. 1996(a). On the modification and characterization of chemical surface properties of activated carbon: in the search of carbons with stable basic properties. Langmuir. 12(18), 4404-4410.

[17.] Menendez, J.A., Radovic, L.R., Xia, B. and Phillips, J. 1996(b). Low-temperature generation of basic carbon surfaces by hydrogen spillover. J Phys Chem. 100(43), 17243-17248.

[18.] Shin, S., Jang, J., Yoon, S. H. and Mochida, I. 1997. A study on the effect of heat treatment on functional groups of pitch based activated carbon fiber using FTIR. Carbon. 35(12), 1739-1743.

[19.] Fanning, P.E. and Vannice, M. A. 1993. A DRIFTS study of formation of surface groups on carbon by oxidation. Carbon. 31(5), 721-730**.**

[20.] Starsinic, M., Taylor, R.L., Walker, P.L. Jr. and Painter P.C. 1983. FTIR studies of saran chars. Carbon. 21(1), 69-74.

[21.] Jagtap, U.B., Panaskar, S.N. and Bapat, V.A. 2010. Evaluation of Antioxidant Capacity and Phenol Content in Jackfruit (Artocarpus heterophyllus Lam) Fruit Pulp. Plant foods for Human nutritio. 65(2), 99-104.

[22.] Appukuttan, P.S. and Basu, D. 1985. Binding site amino acid residues of jack fruit (artocarpus integrifolia) seed lectin: chemical modification and protein difference spectral studies. 7(1), 7-14.

[23.] Schweizer, E.E. and Meeder-Nycz, D. 1977. 2H- and 4H-1-Benzopyrans. In: Chemistry of Heterocyclic Compounds; Ellis, G.P., (Ed.); John Wiley & Sons: New York, 11−139.

[24.] Barroso-Bogeat, A., Alexandre-Franco, M., Fernandez-Gonzalez, C. and Gomez-Serrano, V. 2014. FTIR Analysis of Pyrone and Chromene Structures in Activated Carbon. Energy Fuels. 28(6), 4096-4103.

[25.] Corbett, J.F. and Fooks, A.G. 1967. The chemistry Hydroxy-quinones. Part III. The Reaction of 2,5-Dihydroxy-benzoquinones with Alkali. J. Chem. SOC. (C). 1909-1913.

[26.] Sadykh-Zade, S.I., Ragimov, A.V., Suleimanova, S.S. and Liogon'Kii, V.I. 1972. The polymerization of quinones in an alkaline medium and the structure of the resulting polymers. Polymer Science U.S.S.R. 14(6), 1395-1403.

[27.] Erdtman, H. and Granath, M. 1954. Studies on humic acids. V. The reaction of p-Benzoquinone with alkali. 8, 811-816.

[28.] Sricharoenchaikul, V., Pechyen, C., Aht-ong, D. and Atong, D. 2007. Preparation and Characterization of Activated Carbon from the Pyrolysis of Physic Nut (Jatropha curcas L.) Waste. Energy&Fuels. 22(1), 31-37.

[29.] Yang, T. and Lua, A.C. 2006. Textural and chemical properties of zinc chloride activated carbons prepared from pistachio-nut shells. Mater. Chem. Phys. 100(2), 438-444.

[30.] Jascon, J.M.D. 2012. In: Noval carbon adsorbents, Elsevier publications, Great Britain, ISBN: 978-0-08-097744-7, 80-85.