Activated carbon from corn cob for treating dye waste water

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ABSTRACT

Corn cob which is waste from biopolymer i.e., starchrepresent an interesting alternative as a low cost adsorbent because of its abundant, renewable and biodegradable raw resource and properties such as its chemical stability, oil absorption, surface area, iodine value and high reactivity, resulting from the presence of chemically reactive hydroxyl groups. Corn cob is roasted at high% with low cost chemical as catalyst to reduce time, with temperature control to get 32% yield & certain low cost chemicals areadded for obtaining activated carbon. In order to minimize the energetic cost of the process, the following optimal conditions i.e., 2 N phosphoric acid activating solution, impregnation time of 20 hr, activation temperature at 600° C for 60 min & pH5 are achieved for utilizing in dye wastewater treatment

KEYWORDS

Corn cob;
Phosphoric acid;
Temperature;
Yield;
Oil absorption;
Good surface area;
Iodine value;
Particle size;
Activated carbon;
Methylene blue.

INTRODUCTION

Corn which is naturally occurring material and also it is easily available in plenty in the world. All the corn manufactures in the world used corn starches for several applications except corn cob. Corn cobs contain a considerable reservoir of carbohydrates, most of which are of a polysaccharide nature. These polysaccharides consist principally of cell-wall cellulose and hemicellulose. The term hemicellulose denotes those polysaccharides extractable from plants by aqueous alkali. They are characterized by the type of sugar residue present; thus, D-xylan is a polymer of xylose residues. D-mannan of D-mannose residues, etc. However, the natural occurrence of homoglycansconsiderably less than that of heteroglycans in present-day corn cobs. The heteroglycans usually contain two to four different types of sugar residues, for example, L-arabino-D-xylans and L-arabino-D-glucurono-D-xylans, and have branched structures. The hemicelluloses of corn cobs are mainly heteroxylans. The cell walls of the corn cob contain cellulose bundles which are embedded in an amorphous mass of lignin and polysaccharide material, thus giving a strong and rigid structure

Activated carbon is carbon produced from carbonaceous source materials such as nutshells, peat, wood, coir, lignite, coal, petroleum pitch and maize cob. It can be produced by one of the following processes i.e., physical or chemical activation[5,11]. Before carbonization, the raw material is impregnated with certain chemicals. The chemical is typically an acid, strong base, or a salt[1,6,13,14,17,18], Chemical activation is always preferred

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over physical activation due to the lower temperatures and shorter time need to obtain activated carbon. The absorbent properties of activated carbons are essentially attributed to their large surface area, a high degree of surface reactivity, universal adsorption effect and favourable pore size. However commercial activated carbon being costly has necessitated the development of activated carbon from cheaper materials. The following criteria are considered while choosing carbonaceous raw materials 1. Potential for obtaining high quality carbon 2.presence of inorganics 3.volume and cost 4.storage life 5.low investment 6.high yield. The presence of inorganic and organic pollutants in waste water is on the increase and several of them are not removed by conventional waste water treatment processes and pose problems such as odour, toxicity and foaming

Many industries, such as dyestuffs, textile, paper and plastics, use dyes in order to color their products and also consume substantial volumes of water. As a result, they generate a considerable amount of colored waste water. Due to extensive application, synthetic dyes can cause considerable environmental pollution and are serious health-risk factors. Dyeing industry effluents are one of the most problematic wastewaters to be treated not only for their high chemical oxygen demand, but also for high biological oxygen demand, suspended solids, turbidity, toxic constituents but also for color, which is the first contaminant discernible by the human eye. Dyes may affect the photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to some aquatic life due to the presence of aromatics, metals, etc. in them. Methylene bluedye has high brilliance, intensity of colors, is highly visible even in very low concentration and conventional biological wastewater treatment systems are inefficient in treating dye wastewater.Some of the treated adsorbents have shown good adsorption capacities for methylene blue, Congo red, crystal violet, basic red, etc., but this adsorption process is costly[23]. In order to decrease the cost of treatment, this research article has been made to find the technical feasibility of non-conventional, effective, low-cost adsorbents for dye removal from contaminated water[9,10,19,22].

MATERIALS AND METHODS

Raw materials

Corn cob was obtained from M/s Tirupati Starch and Chemicals, Indore, M.P. India. Phosphoric acid, potassium hydroxide and zinc chloride respectively were of commercial grade

Methods

Figure 1 shows the flow chart of activated carbon from maize cob. Corn cob was cleaned in water and dried completely. It was soaked in 2N respective salts solutions (phosphoric acid, zinc chloride, potassium hydroxide) and further it was also soaked in 1N, 2N, 3 N & 4 N phosphoricacid solutions for 20 hr. After this, excess solution was decanted off and dried at 110 °C for 5 hr. After this, it was taken into a reactor and heated at 180⁰Cfor 14 hr. followed by thermal activation at 600⁰ C for 60 1 hr. under a flow of nitrogen gas (70 ml/min). After this, it was cooled to room temperature immediately. It was grinded in a ball mill for 5hr and taken for analysis.

Physical characterization

pH

pH was found out by systronics expanded pH meter 331 model

Moisture content

The sample was dried at 125 °C for 24 hr. 1 g of the sample was taken in a petri dish. It was spread nicely on the dish. It was then heated at 105⁰ C for 24 hr. The petri-dish was left open during the heating process. After heating, the petri-dish was removed, cooled in a desiccator and weighed.

Moisture content (%) =Loss in weight * 100

Volatile matter

The sample was dried at 125 °C for 24 hr.1 g of the sample was placed in a closed crucible. It was then heated up to 925⁰ C for exactly 7.5 min in a furnace. The crucible was then cooled in desiccators and weighed.

Volatile matter (%) = Loss in weight * 100

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Ash content

The sample was dried at 125 °C for 24 h, and 1 g of the sample was taken in a silica crucible of 10 ml capacity and ignited in a furnace at 900 °C for 5 hr. Then it was allowed to cool to room temperature and weighed.

Ash on Ignition (%) =Weight of the Ash *100

Iodine value of the activated carbon

Iodine value of the activated carbon was measured according to the procedure established by the American Society for Testing and Materials.

Surface area

Quantasorb surface area analyser was used for measuring the surface area of activated carbons. The weighed sample was taken in the cell holder and taken into the sample station. When a stable base line had been established, the signal meter was set to zero and the cells immersed in the liquid nitrogen. As the peak of the adsorption signal was app. 50-60 % on the signal meter, it was set to zero. The integrator was reset and the sample cell immersed in a beaker filled with water until the sample rotometer ball returned to within 1 cm of its starting position when the sample had been returned to zero, the integrator count was recorded. A sample of calibrating gas was injected using a gas tight syringe, the calibration volume and integrators reading were recorded. This experiment was repeated two more times by changing the volume of nitrogen.

Ambient temperature (Pa) =...mm Hg

Sample pressure (Ps) =...mm Hg

Total pressure (Pt) =Pa + Ps= …mm Hg

Vapor pressure (Pg)=...mm Hg

Saturated vapour pressure (P0)= …mm Hg

P0 =Pg+ Pa

Ambient temperature=... K

Molecular weight of adsorbate (Ma) =...28 g

Adsorbate cross sectional area (A_{cs}) = …m^2

Calibration gas weight (X_c)$P_aM_aV_c$

$$= \frac{P_aM_aV_c}{10^4\,T\,*\,6.235}$$

$$X= \frac{X_c\,*\,\text{signal area}}{\text{Calibration area}}$$

A graph was plotted by $\dfrac{1}{X\,[(P0\,/P)\text{-}1]}$ Versus P/P0

Where $P = C_{N2} * P_t$ $X_m = \dfrac{1}{\text{Slope + intercept}}$

$$\text{Surface area (m}^2/\text{g)} = \frac{X_m\,(3.483\,*\,10^5\,)\,m^2}{\text{Weight of the sample (g)}}$$

Oil absorption

The sample was dried for 1 hr at 125 °C and kept in desiccators for 30 min. 1 g of theSample was taken in Whatmann filter paper and placed in a funnel. Dimethyl phthalatewas taken in a burette and added very slowly to it. When it was completely absorbed,the addition stopped and noted the reading.

Oil Absorption (mL/g) = Volume of Dimethyl Phthalate (mL)

Sieve analysis

Test sieve B.S.S.410/43 of mesh size240 were obtained from Geologists Syndicate Limited, Calcutta, West Bengal, India. India.1 kg of the sample was taken into it and shacked exactly for 5 sec. Test sieve B.S.S of mesh size up to 240 was used for this purpose. Particles left in mesh size 240 was taken and weighed. This was repeated three times and the mean was taken.

FTIR

FTIR analysis was made using IPRrestige-21, FTIR-84005, Shimadzu, Corporation, Kyoto,Japan. Sample of 0.1 g was mixed with 1 g of KBr, spectroscopy grade (M/s Merk Darmstadt,Germany), in a mortar. Part of this mix was introduced in a cell connected to a piston of ahydraulic pump giving a compression

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pressure of 15 kP$_a$ / cm^2. The mix was converted to aSolid disc which was placed in an oven at 105^0 C for 4 hr to prevent any interference with anyexisting water vapor or carbon dioxide molecules. Then it was transferred to the FTIR analyzerand a corresponding chromatogram was obtained[4,20].

Preparation of dye solutions

The dye solution of 30 % concentration was prepared by diluting the stock solution with distilled water. The pH adjustment was carried out using 0.1 N HCl solutions. Effect of pH on the adsorption capacity of activated carbon from corn starch was studied in the pH range 3 to 8. The adsorption of methylene blue dye onto activated carbon from corn cob was carried out by shaking 15 % concentration at 30°C in a water bath-cum-mechanical shaker for 50-300 min.

RESULTS AND DISCUSSION

The properties of activated carbons are given in table 1.There is no great differences in properties in pH, % moisture content, % ash content, % volatile matter, % fixed carbon, and %yield. From TABLE 1, it is concluded that characterization studies clearly indicate that the activated carbon obtained by phosphoric acid process than the other two processes shows high surface area,oil absorption and iodine value which is directly related to porosity. In chemical activation, different activating agents are expected to significantly affect the extent of activation. In the present study, activating solutions with phosphoric acid, Potassium Hy-

droxide and zinc chloride andpotassium hydroxideare evaluated and compared. The concentrations of various chemical activating agents are fixed at 2 N, the impregnation time for these agents is maintained as 20 hr, activation temperature 600^0 C and activating time 60 min. The oil absorption, surface area and iodine values of activated carbons change significantly with activating agents. Activated carbon with phosphoric acid activating solution is quite high as it penetrates into corn cob is fast and high

TABLE 1 : Properties of activated carbons

SL.	Properties	H$_3$PO$_4$	ZnCl$_2$	KOH
1	pH	05.90	06.40	06.00
2	Moisture content (%)	13.40	11.50	12.00
3	Ash content (%)	09.16	11.89	13.40
4	Volatile matter (%)	02.80	08.40	07.90
5	Fixed carbon (%)	74.80	74.70	74.50
6	Oil absorption g/ml	01.95	01.45	01.60
7	Surface area (m^2/g)	660.00	502.25	550.00
8	Yield (%)	32.00	31.90	30.85
9	Particle size (%) 240	98.50	97.60	97.10
10	Iodine value	645.80	585.50	545.40

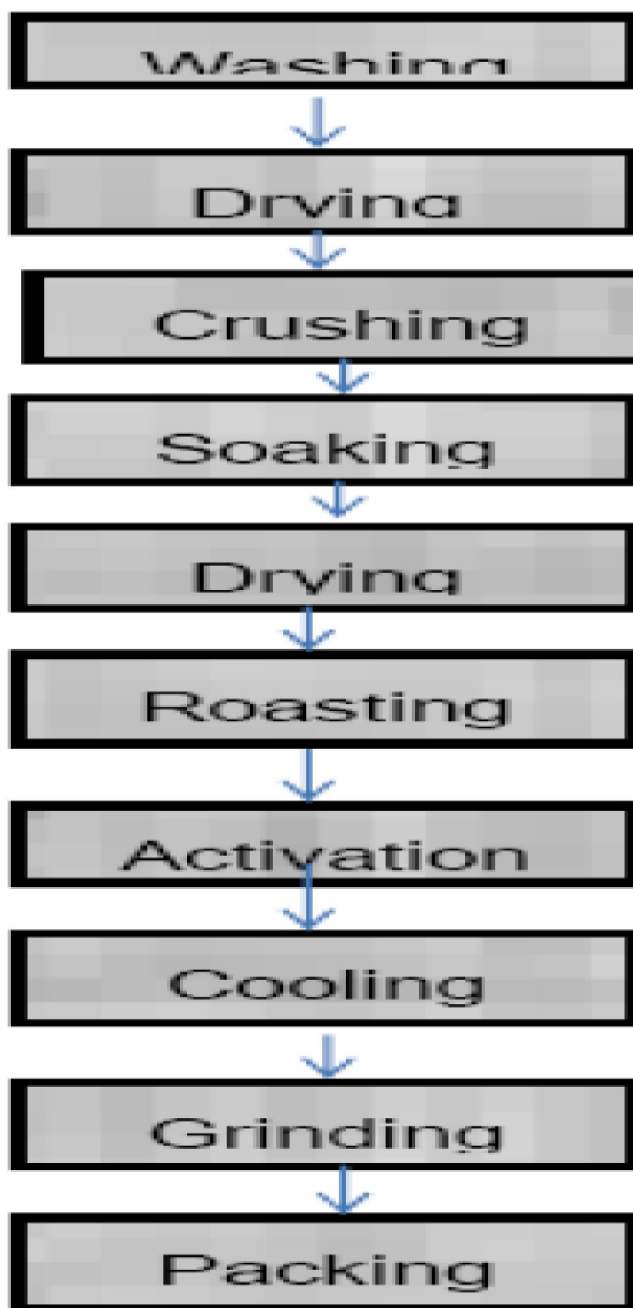**Figure 1 : Flow chart of activated carbon from corn cob**

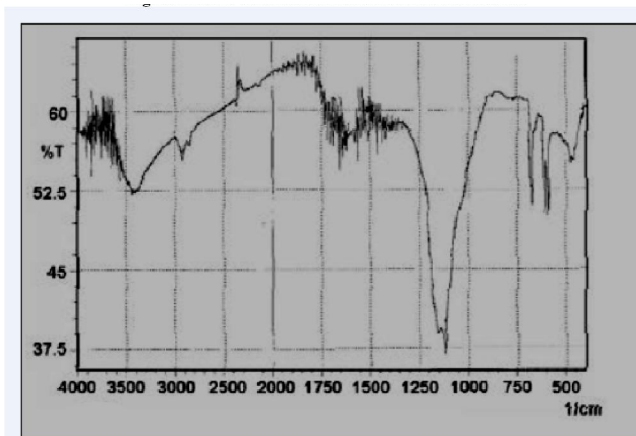*Current Research Paper*

Figure 2 : FTIR spectrum of activated carbon from corn cob

FTIR analysis

The FTIR spectroscopic study of the produced carbon is shown in Figure 2. The sample shows four major absorption bands at 2900-3500 cm⁻¹, 1300-1750 cm⁻¹, 1000-1250 cm⁻¹ and 450-750cm⁻¹. A wide band with two maximum peaks can be noticed at 2930 and 3450 cm⁻¹. The band at 3450 cm⁻¹ is due to the absorption of water molecules as result of an O-H stretching mode of hydroxyl groups and adsorbed water, while the band at 2930 cm⁻¹ is attributed to C-H interaction with the surface of the carbon. However, it must be indicated that the bands in the range of 3200-3650 cm⁻¹ have also been attributed to the hydrogen-bonded OH group of alcohols and phenols. In the region 1300-1750 cm⁻¹, amides can be distinguished on surface of the activated carbon which has two peaks at 1640 and 1450 cm⁻¹. These functional groups were obtained during the activation process as a result of the presence of ammonia and primary amines that usually exist in the carbon. Moreover, the band at 1500 cm⁻¹ may be attributed to the aromatic carbon–carbon stretching vibration. The two peaks at 1125-1150 cm⁻¹ yield the fingerprint of this carbon. The sharp absorption band at 1125 cm⁻¹ is ascribed to either Si-O or C-O stretching in alcohol, ether or hydroxyl groups. The band at 1150 cm⁻¹ can also be associated with ether C-O -symmetric and asymmetric stretching vibration (-C-O-C- ring). This band could also be attributed to the anti-symmetrical Si-O -Si stretching mode as a result of existing alumina and silica containing minerals within the corn starch samples. The region 450-750 cm⁻¹ shows two bands in the 480 and 485 cm⁻¹ which

are associated with the in-plane and out-of-plane aromatic ring deformation vibrations. Peaks at 598 and 680 cm⁻¹ are assigned to the out-of-plane C-H bending mode. These spectra are also suggested to be due to alkaline groups of cyclic ketones and their derivatives added during activation.

Effect of concentration of phosphoric acid solution used for producing activated carbons

TABLE 2 : Effect of concentration of H_3PO_4 solutionson iodine value of activated carbon

Conc. of H_3PO_4 (N)	Iodine value (mg/g)
1	692.4
2	765.8
3	607.8

TABLE 2 shows the effect of different concentration of phosphoric acid solution on iodine value. The iodine value of activated carbon is 765.8mg/ g maximum only at 2N concentration indicating good surface area and porosity. When the concentration decreases to 1 N, the iodine value is relatively low because of insufficient phosphoric acid to react with corn cob to efficiently create the internal pore structures. However, if the concentration of phosphoric acid is as high as 3N or more, the micro pore structure of corn starch deteriorated due to excessive activating solution.

Effect of time of impregnation on activated carbon products

TABLE 3 : Effect of impregnation time of H3PO4 solutionson iodine valueof activated carbon

Impregnation time (hr)	Iodine value(mg/g)
10	502.7
15	554.8
20	665.8
25	528.9

TABLE 3 shows the time of impregnation of phosphoric acid solutions on corn starches. The iodine values of activated carbon increased gradually with time of impregnation, and leveled off after 20 hr. Long impregnation time would promote the diffusion of phosphoric acid in corn cob. When the time is extended to 20 hr, equilibrium is attained in the mixture of corn cob

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and phosphoric acid solution. Hence, the impregnation time of 20 hr is required.

Effect of activation temperature on activated carbon

TABLE 4 : Effect of activation temperature on iodine value of activated carbon

Activation temperature^0 C	Iodine value(mg/g)
500	543.2
600	765.8
700	589.9
800	561.6

TABLE 4 shows the effect of activation temperature on activated carbons. The activation temperature is a very influential parameter on the pore structure of activated carbon, which determines the adsorption capacity. The variation in iodine values of activated carbon product is investigated as a function of activation temperature. Corn cob is used as raw material and activation time is fixed at 60 min. As shown in Figure 6, the iodine value increases progressively with activation temperature, and then decreases when the temperature exceeded 600^0 C. At higher temperature, the pore walls between adjacent pores are probably destroyed and the micro-pores are destructed which led to the decrease in iodine value of the activated carbon. Thus, it can be concluded that the optimum temperature for the production of activated carbons from corn cob is approximately 600^{0}C.

Effect of activation time on activated carbon products

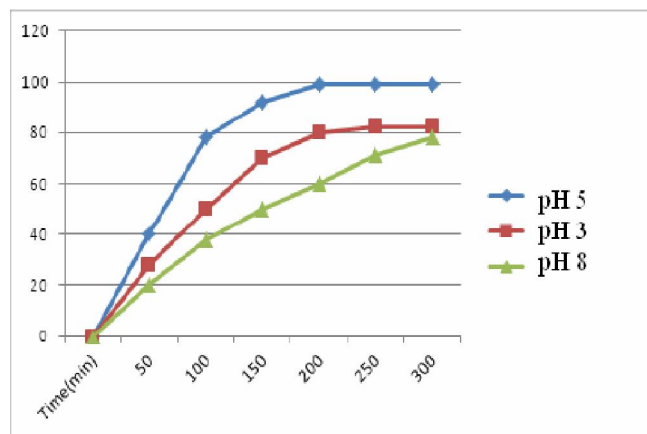The variations in iodine value of activated carbon

Figure 3 : Effect on pH on % methylene blue dye removal

produced from corn starch are shown in TABLE 5. The iodine values are measured as 690.9 mg/ g and 765.8mg/ g after 30 min and 60 min. of activation time, respectively. Thereafter, the iodine value gradually dropped to a value of 574.3 mg/g at 3 hr. The decrease in iodine value for the time period of 1–3 hr is considered to be due to the extended activation of product, resulting in the conversion of some micro pores into meso- pores and meso- pores into macro- pores. This trend indicates that the activation time of 60 min. is optimum[7,8,12,15,16,18,21].

TABLE 5 : Effect of activation temperature on iodine value of activated carbon

Activation time(min)	Iodine value(mg/g)
30	690.9
60	766.2
90	704.6
120	616.9
180	574.8

Effect of pH

TABLE 3 shows influence of time & pH on % dye removal at 30 % concentration of dye solutions. This trend may be explained on the basis of the fact that at pH below 6, the methylene blue ions readily enter into the pore structure of activated carbon from corn cob whereas at pH beyond 6, the zwitter ionic form of methylene blue in water aggregated to form a dimer, which was unable to enter into the pores. It shows that rate of methylene uptake was rapid in the initial 75-100 min. This became slower during 100 to 200 min and attaining equilibrium in 150 min. The percent removal followed the same pattern and increases from 48 to 99.5% when time increased from 75 to 200 min. This is expected because a large number of surface sites are available for adsorption at the initial stages and after a lapse of time, the remaining surface sites are difficult to occupy because of repulsion between methylene blue molecules of the solid and bulk phases

CONCLUSIONS

Corn cob which is naturally occurring material and also it is easily available in plenty in the world. All the corn manufactures in the world used corn starches for

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several applications except corn cob.The results of this study show that it is feasible to prepare activated carbon from corn cob by direct chemical activation. An activation with phosphoric acid solution from corn cob produces activated carbon for dye waste water treatment than with potassium hydroxide and zinc chloride solutions.Adsorption of impurities from dye waste water onto activated carbon prepared from corn cob by phosphoric acid process with low investment is found to be low cost absorbent, free from pollution, high profit margin & save life

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REFERENCES

[1] Ahmedna, Marshall, Rao; Production of granular activated carbons from select agricultural by-products and evaluation of their physical, chemical and adsorption properties. BiosourceTechnology: 71, 113-123 **(2000)**.

[2] Alonso, Tascon; Porous texture of activated carbons, **(2003)**.

[3] Prepared by phosphoric acid activation of apple pulp. Carbon, **39**, 1103-1116.

[4] Calzaferri, Imhof; In situ attenuated total reflection FTIR investigations of H2O, HSiCl3 and Co2 (CO)8 on ZnSe in the range 600–4000 cm"1. SpectrochimicaActa Part A, Molecular and Biomolecular Spectroscopy, **52**, 23-28 **(1996)**.

[5] El- Hendawy; Influence of HNO3 oxidation on the structured and adsorptive properties of corncob activated carbon.Carbon, **41**, 713-722 **(2003)**.

[6] Elsheikh, Newman, Al-Daffaee, Phull, Crosswell; Characterization of activated carbon prepared from a single cultivar of Jordanian olive stones by chemical and physicochemical techniques. J. Anal. Appl. Pyrolysis, **30**, 1-16 **(2003)**.

[7] Garcia, Alonso, Tascon; Porous texture of activated carbons prepared by phosphoric acid activation of apple pulp. Carbon, **39**, 1103-1116 **(2003)**.

[8] Guo, Lua; Textural and chemical characterizations of activated carbon prepared from oil palm stone with H2SO4 and KOH impregnation. Microporous and Mesoporous Materials, **32**, 111-117 **(1999)**.

[9] Hu, Vansant; E F A new composite adsorbent produced by chemical activation of elutrilithe with zinc chloride. J.Colloid Interface Sci., **176(2)**, 422–431 **(1995)**.

[10] Jeyaseelan, Lu; Development of adsorbent/catalyst from activated carbon Production from biological sludge by chemical activation with ZnCl2 and H2SO4. Environmental Technology, **17**, 667-672 **(1999)**.

[11] Kadirvelu, Kavipriya, Karthika, Radhika, Vennilamani, Pattabhi; Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. Bioresource Technology, **87**, 129–132 **(2003)**.

[12] Khalili, Campbell Sandi, Gola; Production of micro and mesoporous activated carbon from paper mill sludge, I: Effect of zinc chloride activation.Carbon, **38**, 1905- 1915 **(2000)**.

[13] Kim, Sohn, Kim, Sohn, Kwon; Production of granular activated carbon from waste walnut shell and its adsorption characteristics for Cu2þ ion. J.Hazard.Mater, **85(3)**, 301–315 **(2001)**.

[14] Laine, Calafat, Labady; Preparation and characterization of activated carbons from coconut shell impregnatedted with phosphoric acid. Carbon, **27**, 191-195 **(1989)**.

[15] Mikhail, Brunauer, EBodor; Investigations of a complete pore structure analysis I. Analysis of microspores. J.Colloid Interface Sci., **26**, 45–53 **(1968)**.

[16] Molina-Sabio,Gonzalez, Rodriguez-Reinoso, Sepulveda-Escribano; Effect of steam and carbon dioxide activation in the micropore size distribution of activated carbon. Carbon, **344**, 505–5096 **(1996)**.

[17] R.M.Narbaitz, A.Karimi-Jashni; Electrochemical regeneration of granular activated carbons loaded with phenol and natural organic matter. Environmental Technology, **30(1)**, 27–36 **(2009)**.

[18] A.M.Puziy, O.I.Poddubnaya, A.Matinez-Alonso, F.Suarez-Garcia, J.M.D.Tascon; Characterization of synthetic carbon activated with phosphoric acid. Applied Surface Science, **200**, 196-202 **(2002)**.

[19] Rodriguez-Reinoso, M.Molina-Sabio, M.T.Gonzalez; The use of steam and CO2asactivating agents in the preparation of activated carbons. Carbon, **33(1)**, 15–23 **(1995)**.

Current Research Paper

[20] G.Socrates; Infrared Characteristic Group Frequencies.John Wiley &Sons. New York, USA **(1994)**.

[21] R.Torregrosa-Macia, J.M.Martin-Martinez, M.C.Mittelmeijer-Hazeleger; Porous texture of activated carbons modified with carbohydrates. Carbon, **35(4)**, 447–453 **(1997)**.

[22] X.Wang, N.Zhu, B.Yin; Preparation of sludge-based activated carbon and its application in dye wastewater treatment. J.Hazard.Mater, **153(1–2)**, 22–27 **(2008)**.

[23] Z.Yue, J.Economy, G.Bordson; Preparation and characterization of NaOH-activated carbons from phenolic resin. J.Mater.Chem, **16(15)**, 1456–1461 **(2006)**.