International Journal of Engineering Science Invention
ISSN (Online): 2319 – 6734, ISSN (Print): 2319 – 6726
www.ijesi.org Volume 2 Issue 9‖ September 2013 ‖ PP.45-53

Activated carbon from corn starch for treating dye waste water

N Samson Maria Louis[1 *], S Sudha[2]

[1]*Asst.Prof. Department of Science & Humanities (Chemistry), Sri Ramakrishna Institute of Technology, Pachapalayam,Coimbatore-641010,Tamilnadu,India.*
[2]*Asst. Prof. Department of Science & Humanities (Chemistry), Sri Ramakrishna Institute of Technology, Pachapalayam, Coimbatore-641010, Tamilnadu, India*

ABSTRACT: *Corn starch which is biopolymer, represent an interesting alternative as a low cost adsorbent because of its abundant, renewable, 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 in its polymer chains. Corn starch is roasted at high% with low cost chemical as catalyst to reduce time, with temperature control to get 32% yield & certain low cost chemicals are added for obtaining activated carbon. In order to minimize the energetic cost of the process, the following optimal conditions i.e., 2 N Zinc Chloride activating solution, impregnation time of 20 hr, activation temperature at 600^{O} C for 60 min & pH 5 are achieved for utilizing in dye waste water treatment*

KEYWORDS: *activated carbon, corn starch, high % chemical as catalyst, surface area, temperature*

I. INTRODUCTION

Corn which is naturally occurring material and also it is easily available in plenty in the world [1]. All the corn manufactures in the world used corn starches for several applications except waste water treatment. Starch is a carbohydrate consisting of a large number of glucose units joined by glycosides bonds. This polysaccharide is produced by all green plants as an energy store. It is contained in large amounts in such staple foods as potatoes, wheat, corn, rice, and cassava. Pure starch is a white, tasteless and odourless powder that is insoluble in cold water or alcohol. It consists of two types of molecules i.e., the linear amylose and the branched amylopectin. Depending on the plant, starch generally contains 20 to 25% amylose and 75 to 80% amylopectin by weight. Glycogen, the glucose store of animals, is a more branched version of amylopectin. Starch is processed to produce many of the sugars in processed foods. Dissolving starch in warm water gives wheat paste, which can be used as a thickening, stiffening or gluing agent. The biggest industrial non-food use of starch is as adhesive in the papermaking process and corrugated board. Further, it finds application in the manufacture of various adhesives or glues for book-binding, wallpaper adhesives, paper sack production, tube winding, gummed paper, envelope adhesives, school glues and bottle labelling. Textile chemicals from starch are used to reduce breaking of yarns during weaving. Starch is mainly used to size cotton based yarns. Modified starch is also used as textile printing thickener. Starch is used to produce various bio plastics, synthetic polymers that are biodegradable. Powdered corn starch is used as a substitute for talcum powder, and similarly in other health and beauty products .In oil exploration, starch is used to adjust the viscosity of drilling fluid, which is used to lubricate the drill head and suspend the grinding residue in petroleum extraction. Glucose from starch can be further fermented to ethanol using wet & dry milling processes.

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[2,3].Before carbonization, the raw material is impregnated with certain chemicals. The chemical is typically an acid, strong base, or a salt [4-8].Chemical activation is always preferred over physical activation due to the lower temperatures and shorter time need to obtain activated carbon. In addition, activated carbon can be used in household. Its major household usage is found in refrigerators. 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 inorganic 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 wastewater. It is recognized that public perception of water quality is greatly influenced by the color. Color is the first contaminant to be recognized in wastewater. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable. Due to extensive application, synthetic dyes can cause considerable environmental pollution and are serious health-risk factors. 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. Some of the treated adsorbents have shown good adsorption capacities for methylene blue, Congo red, crystal violet, RB, basic red, etc., but this adsorption process is highly pH dependent, and the pH of the medium plays an important role in the treatment process [9].They are used extensively in textile industries regarding favorable characteristics of bright color; water fast, simple application techniques with low energy consumption. Basic dyes have high brilliance and intensity of colors and are highly visible even in very low concentration. Due to the chemical stability and low biodegradability of these, conventional biological wastewater treatment systems are inefficient in treating dye wastewater. Most commercial systems currently use activated carbon as absorbent to remove dyes in wastewater because of its excellent adsorption ability.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 [10-13].

II. MATERIALS AND METHODS

2.1. Raw materials

Corn starch was obtained from M/s Tirupati Starch and Chemicals, Indore, M.P. India. Hydrochloric acid, Zinc Chloride, Potassium Hydroxide and Potassium Chloride respectively were of commercial grade

2.2. Methods

Corn starch was soaked in 2N respective salts solutions (Zinc chloride, Potassium Hydroxide and Potassium Chloride) and further it was also soaked in 1N, 2N, 3 N & 4 N Zinc Chloride solutions for 20 hr. After this, excess solution was decanted off and dried at 110^0 C for 5 hr. Then it was mixed with 3.2% mixture containing equal volume of hydrochloric acid & water. After this, it was taken into a reactor and heated at 180^0Cfor 14 hr. followed by thermal activation at 600^0 C for 60 min. 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.

2.3. Physical characterization

2.3.1. pH

pH was found out by systronics expanded pH meter 331 model

2.3.2. 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 105^0 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

2.3.3. 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 925^0 C for exactly 7.5 min in a furnace. The crucible was then cooled in a desiccator and weighed.
Volatile matter (%) = Loss in weight * 100

2.3.4. 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

2.3. 5. Iodine value of activated carbon

Iodine value of activated carbon was measured according to the procedure established by the American Society for Testing and Materials (ASTM 2006).

2.3.6. Surface area

Quantasorb surface area analyser was used for measuring the surface area of activated carbons [14].

2.3.7. Oil absorption

The sample was dried for 1 hr at 125 °C and kept in desiccators for 30 min. 1 g of the sample was taken in Whatmann filter paper and placed in a funnel. Dimethyl phthalate was 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)

2.3. 8. Sieve analysis

Test sieve B.S.S .410/43 of mesh size240 were obtained from Geologists Syndicate Limited, Calcutta, West Bengal, India. Sieve analysis was done by sieve shaker (Lynx) M/s Lawrence & Mayo, 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 value was taken

2.3.9. 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 a hydraulic pump giving a compression pressure of 15 kP_a / cm^2. The mix was converted to a solid disc which was placed in an oven at 105^0 C for 4 hr to prevent any interference with any existing water vapor or carbon dioxide molecules. Then it was transferred to the FTIR analyzer and a corresponding chromatogram was obtained [15].

2.3.10. 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 RB dye onto activated carbon from corn starch was carried out by shaking 15 % concentration at 30°C in a water bath-cum-mechanical shaker for 50-300 min.

III. 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 and figs. 1,2,3, it is concluded that characterization studies clearly indicate that the activated carbon obtained by zinc chloride 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 Zinc Chloride, Potassium Hydroxide and Potassium Chloride are 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 Zinc Chloride activating solution is quite high as it penetrates into corn starch is fast and high

3.1. FTIR analysis

The FTIR spectroscopic study of the produced carbon is shown in Fig. 4. 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 at3450 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 3200-3650cm^{-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 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.

3.2. Effect of concentration of Zinc Chloride solution used for producing activated carbons

Table 2 and fig.5 show the effect of different concentration of Zinc Chloride 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 Zinc Chloride to react with corn starch to efficiently create the internal pore structures. However, if the concentration of Zinc Chloride is as high as 3N or more, the micro pore structure of corn starch deteriorated due to excessive activating solution.

3.3. Effect of time of impregnation on corn starch

Table 3 and fig.6 show the time of impregnation of Zinc Chloride 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 Zinc Chloride in corn starch. When the time is extended to 20 hr, equilibrium is attained in the mixture of corn starch and Zinc Chloride solution. Hence, the impregnation time of 20 hr is required.

3.4. Effect of activation temperature on activated carbon

Table 4 and fig. 7show 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 starch 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 starch is approximately 600^0C.

3.5. Effect of activation time on activated carbon products

The variations in iodine value of activated carbon produced from corn starch are shown in Table 5 & fig. 8. 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 [16-23]

3.6. Effect of pH

Fig. 9 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 RB ions readily enter into the pore structure of activated carbon from corn starch whereas at pH beyond 6, the zwitter ionic form of RB in water aggregated to form a dimer, which was unable to enter into the pores. It shows that rate of RB 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 RB molecules of the solid and bulk phases

IV. CONCLUSIONS

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 waste water treatment.The results of this study show that it is feasible to prepare activated carbon from corn starch by direct chemical activation. An activation with Zinc Chloride solution from corn starch produces activated carbon for dye waste water treatment than with Potassium Hydroxide and Potassium Chloride solutions.Adsorption of impurities from dye waste water onto activated carbon prepared from corn starch by Zinc Chloride process is found to be low cost absorbent with also low investment.

V. ACKNOWLEDGEMENTS

We wish to express our sincere thanks and gratitude to TRUSTEE, Principal and other members of Sri Ramakrishna Institute of Technology, Coimbatore, India for providing help throughout the course of this research paper

REFERENCES

[1]. James Bemiller, Roy Lester Whistler&N Roy Lester Whistler, Starch Chemistry and Technology, Academic Press MA 01803 USA.ISBN: 0127462759

[2]. Kadirvelu, K.Kavipriya, M.Karthika, C.Radhika, M .Vennilamani, N.&Pattabhi, S. Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions Bioresource Technology, 8(2003), 129–132.

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

[4]. Laine, J.Calafat, A.&Labady, M. Preparation and characterization of activated carbons from coconut Shell impregnatedted with phosphoric acid. Carbon, 27(1989), 191-195.

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

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

[7]. Ahmedna, M. Marshall, W. E .&Rao, R.M.Production of granular activated carbons from select agricultural by-products and evaluation of their physical, chemical and adsorption properties. BiosourceTechnology,71(2000), 113-123

[8]. Elsheikh, A.Newman, A. Al-Daffaee, H.Phull, S.Crosswell, N.Characterization of activated carbon prepared from a single cultivar of Jordanian olive stones by chemical and physicochemical techniques.Journal of Analytical Applied Pyrolysis, 30(2003), 1-16

[9]. Kim, J.W. Sohn, M. H.Kim , D. S.Sohn, S. M.& Kwon, Y. S.Production of granular activated carbon from waste walnut shell and its adsorption characteristics for Cu2þ ion.JournalofHazardaous Materials,85(3(2001), 301–315.

[10]. Yue, Z. Economy, J. &Bordson, G. Preparation and characterization of NaOH-activated carbons from Phenolic resin.Journal Materials Chemistry16(15)(2006), 1456–1461.

[11]. Wang,X,.Zhu, N. & Yin, B. Preparation of sludge-based activated carbon and its application in dye Waste water treatment.JournalHazardaous. Materials , 153(1–2)(2008), 22–27

[12]. Hu, Z.&Vansant, E. F.A new composite adsorbent produced by chemical activation of elutrilithe with zinc chloride.Journal Colloid Interface Science, 176(2)(1995), 422–431.

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

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

[15]. N.Samson Maria Louis, Sabu Thomas, Effect of rice husk ash on mechanical properties of low density polyethylene, Journal of scientific & Industrial Research, 71(2012)

[16]. Socrates, G.Infrared Characteristic Group Frequencies .4 thedn.,John Wiley &Sons. New York, USA Khalili, N. R. Campbell Sandi, G.&Gola,J.Production of micro and mesoporous activated carbon from paper mill sludge, I: Effect of zinc chloride activation.Carbon, 38(2000),1905- 1915.

[17]. A. M.Tascon, J. M. D.Porous texture of activated carbons Prepared by phosphoric acid activation of apple pulp. Carbon, 39 9(2003), 1103-1116.

[18]. Molina-Sabio ,M. T. Gonzalez ,F. Rodriguez-Reinoso ,A . & Sepulveda-Escribano.Effect of steam and Carbon dioxide activation in the micropore size distribution of activated carbon.Carbon, 344(1996), 505–5096

[19]. Guo, J. Lua,A.Textural and chemical characterizations of activated carbon prepared from oil palm stone With H2SO4 and KOH impregnation.Microporous and Mesoporous Materials,32(1999), 111-117.

[20]. Garcia, F. S .Alonso, A. M .Tascon, J. M .D. Porous texture of activated carbons prepared by phosphoric acid activation of apple pulp. Carbon39,(2003)1103-1116.

[21]. P. J. M.Carrott, R .A. Roberts, K. S W Sing,Standard nitrogen adsorption data for nonporous carbons. Carbon, 25(1996), 769–770.

[22]. R. S. Mikhail, S. Brunauer ,E.EBodor,Investigations of a complete pore structure analysis I. Analysis of microspores. Journal Colloid InterfaceScience, 26(1968), 45–53

[23]. R .Torregrosa-Macia, J. M. Martin-Martinez, M .C .Mittelmeijer-Hazeleg, Porous texture of activated carbons modified with carbohydrates.Carbon,35 (4)(1995), 447–453

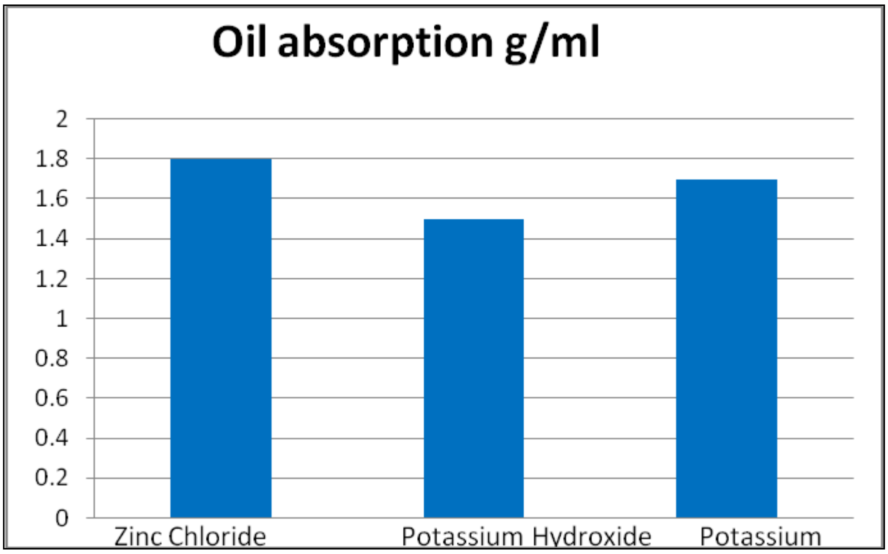

Fig.1 Oil absorption vs. different activating solutions

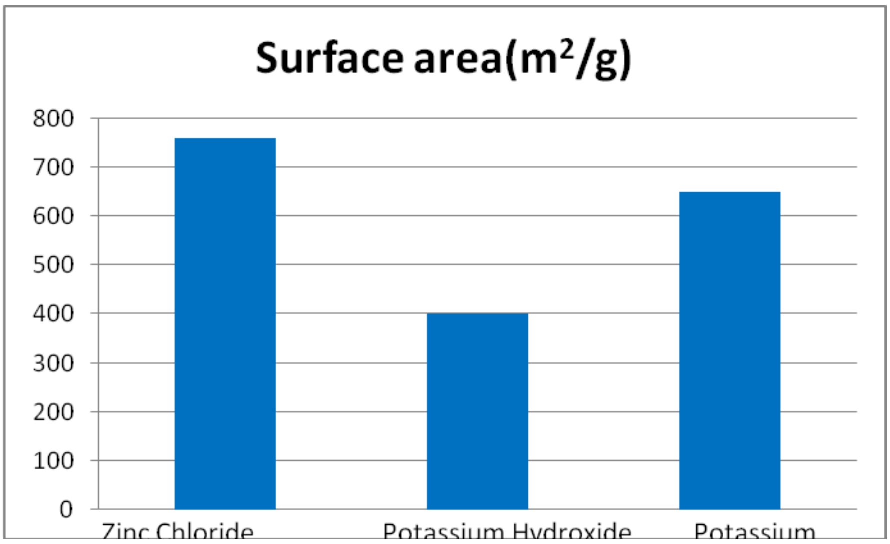

Fig .2 Surface area vs. different activating solutions

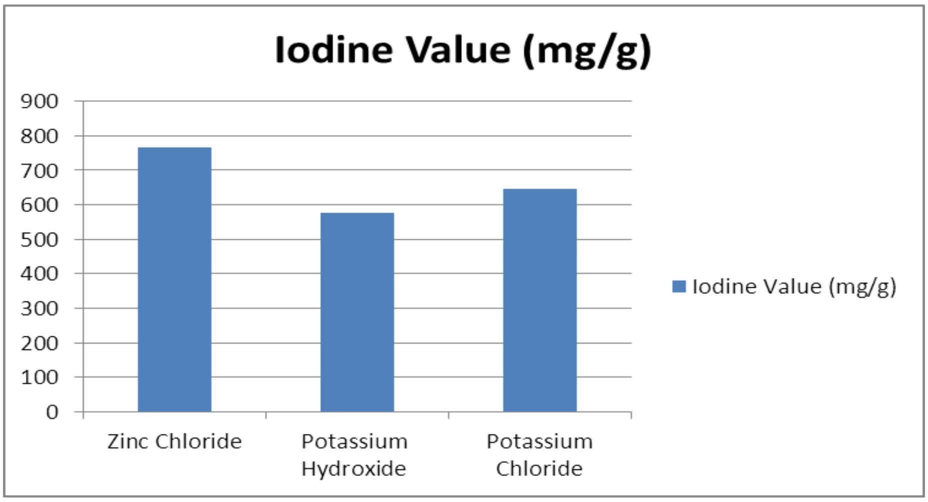

Fig. 3 Iodine value vs. different activating solutions

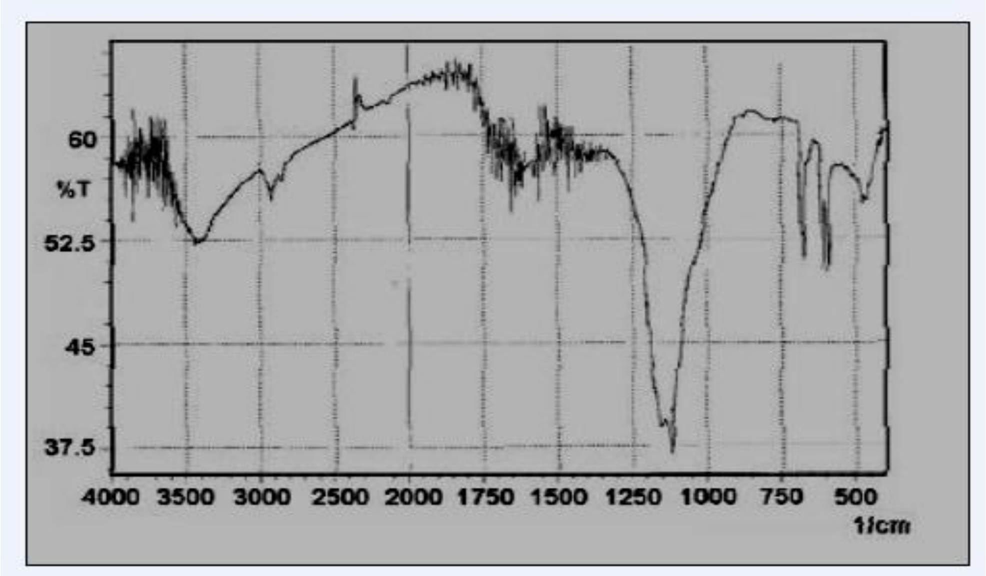

Fig. 4 FTIR spectrum of activated carbon from corn starch

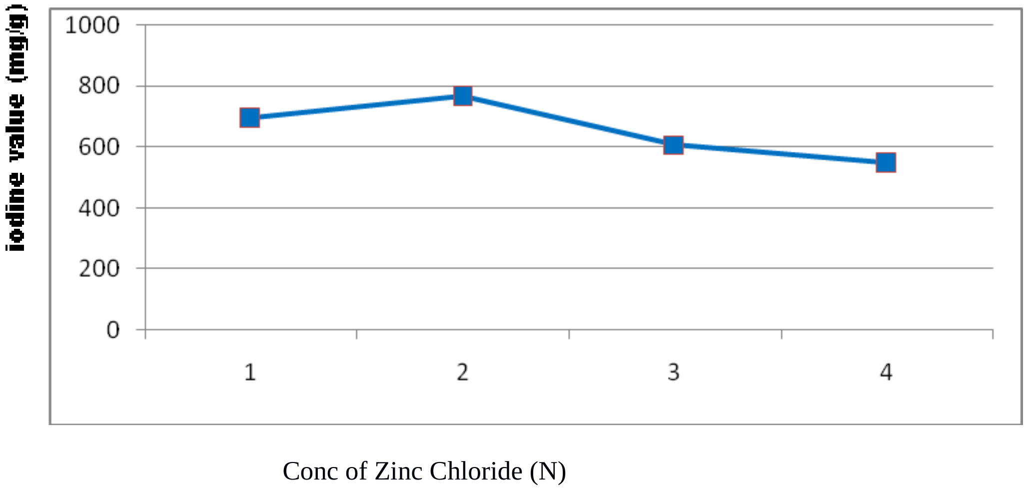

Fig.5 Effect of different concentrations of Zinc Chloride solutions on iodine value

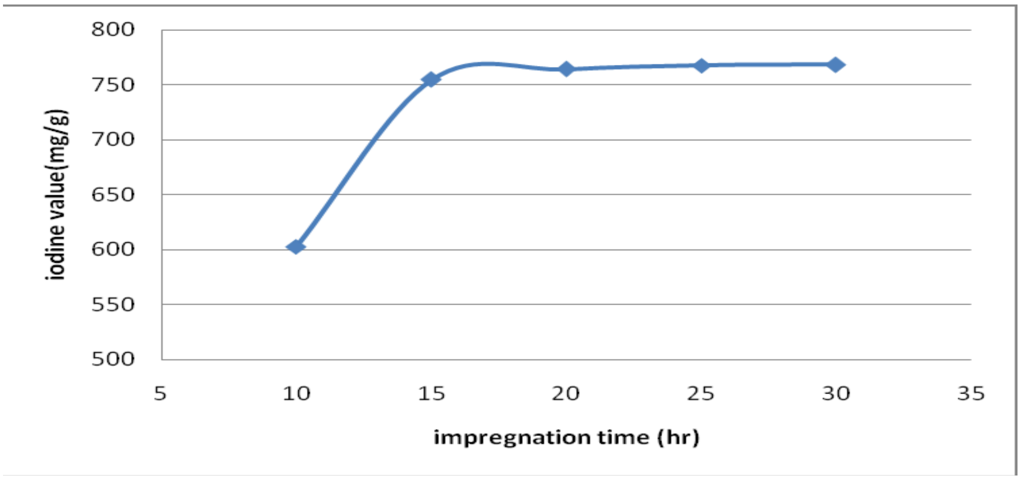

Fig. 6 Effect of impregnation time on iodine value

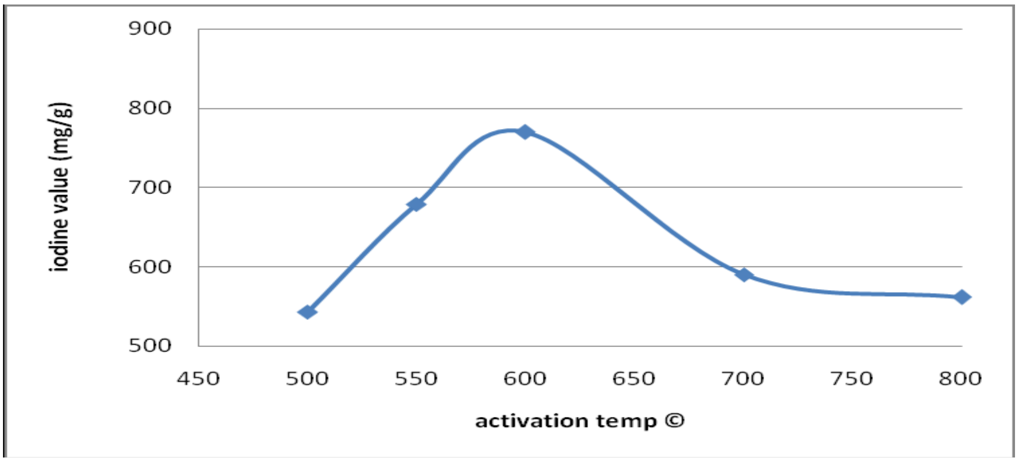

Fig.7 Effect of activation temperature on iodine value of activated carbon

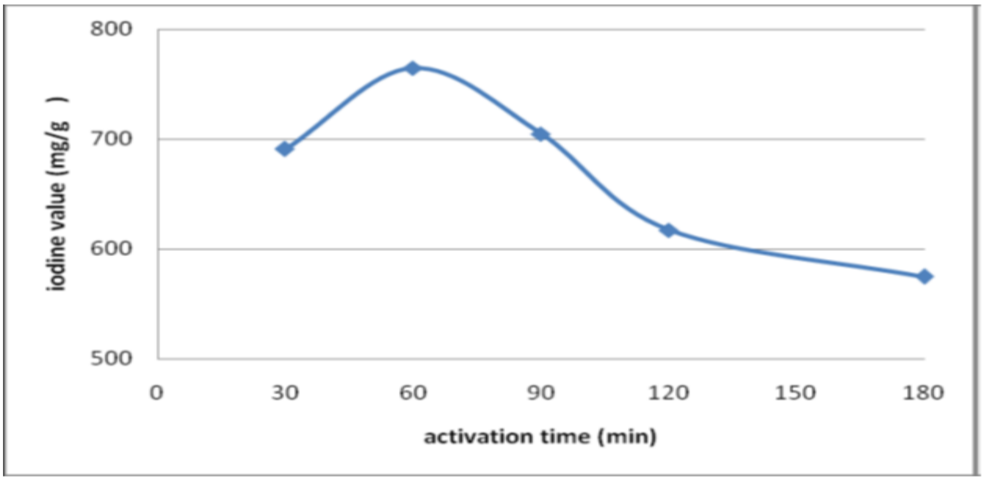

Fig. 8 Effect of activation time on iodine value of activated carbon

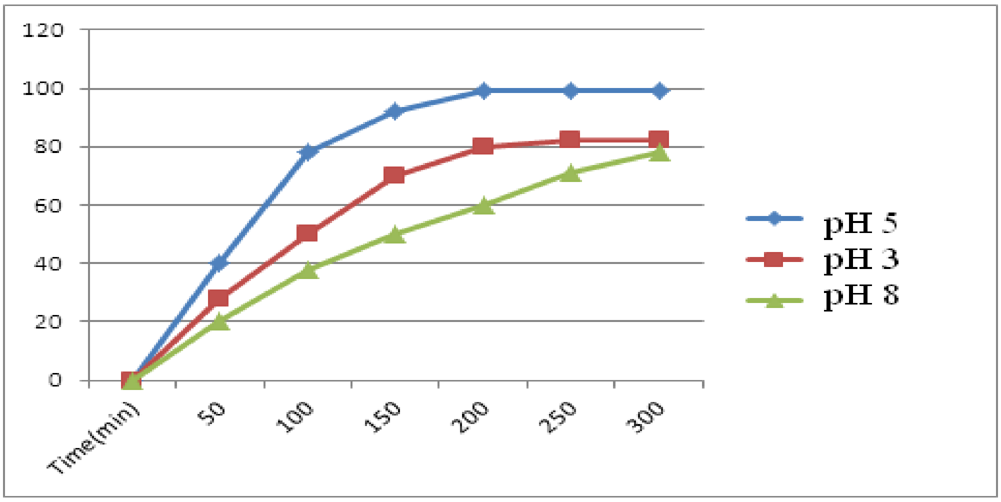

Fig. 9 Influence of time & pH on % dye removal at 30 % concentration of dye solutions

Table1 Properties of activated carbons

SL.	Properties	Zinc Chloride	Potassium Hydroxide	Potassium
1	pH	5.90	6.50	6.90
2	Moisture content (%)	13.40	11.80	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	72.70	73.50
6	Oil absorption g/ml	01.80	01.50	01.60
7	Surface area (m^2/g)	760	402	650
8	Yield (%)	32.00	31.90	30.85
9	Particle size (%) 240 mesh	98.50	97.60	97.10
10	Iodine value (gm./g)	765.8	575.5	645.4

Table 2 Effect of concentration of Zinc Chloride solutions on iodine value

Conc. of Zinc Chloride (N)	Iodine value (mg/g)
1	692.4
2	765.8
3	607.8
4	547.5

Table 3 Effect of impregnation time on iodine value of Zinc Chloride solutions

Impregnation time (hr)	Iodine value(mg/g)
10	602.7
15	754.8
20	765.8
25	768.9
30	768.5

Table 4 Effect of activation temperature on iodine value of activated carbon

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

Table 5 Effect of activation time on iodine value of activated carbon products

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