



Tests for Evaluating the Efficacy of Phosphoric Acid Activated Charcoals from Two Biomasses

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ABSTRACT

Good quality activated charcoals were prepared from areca nutshell and coconut shell using phosphoric acid as a chemical activating agent at 400°C. Physico-chemical properties like iodine number, methylene blue number, and surface area of two activated charcoals were measured to assess the porous nature. A special test called acetic acid number was devised to understand the quality of functional groups on charcoal surfaces. Proximate analysis and physical properties of the two activated charcoals closely matched those of a commercial sample, confirming the good quality of samples prepared in the laboratory. Adsorption of isolated caramel from waste stream obeyed Freundlich isotherm, and the data could be explained based on the physisorption of large size molecules on the walls of mesoporous solid surface. Adsorption of methylene blue involving Coulombic attraction towards the areca nut shell-derived activated charcoal could be predicted and confirmed based on the acetic acid number for the first time.

INTRODUCTION

With the rapid advancement in science and technology, the standard of living of humankind has reached new high horizons. At the same time, water, air, and land pollution has also reached intolerable limits exposing humankind to the hazards of ecological calamities. The major problem faced by people of all nations, especially developing countries, is water pollution. Alcohol distilleries and dyestuff-based industries are the major polluters of water because their effluent streams are highly colored. Distilleries produce colored effluent called spent wash to 7-12 liters per liter of alcohol produced. The spent wash is highly toxic and contains high BOD (55×10^3) and COD (approximately $110-140 \times 10^3$) ppm. High BOD and COD associated with spent wash are due to bio-refractory components, like melanoidin, caramels, anthocyanins, tannins, lignins, and different xenobiotic compounds (Pandey et al. 2003, Tiwari et al. 2007).

The textile industry is the major consumer of dyes, and about 10-15% of the dyes used come out through effluent streams (Zolliger 1987, Hai et al. 2007, Hussain 2006). In addition to the textile industry, dye manufacturing, paper and

pulp, tannery, and paint industries produce large quantities of effluent-containing dyes. These effluents are considered objectionable because they cause carcinogenic skin irritation (Christe 2007). Dyestuffs are difficult to decompose biologically because they are highly structured polymeric (Namasivayam et al. 2001). In the case of distillery effluent, even after initial biological treatment, coloring compounds are not removed even though BOD and COD are reduced to a certain extent. Thus, removing coloring material is the major problem in both effluents. Many methods are popular for the color removal of this wastewater, viz. floatation, chemical coagulation, chemical oxidation, and adsorption (Gupta et al. 2000). Among these, adsorption has been very popular for color removal from wastewater because of its many advantages. These are: it is simple in design, comparatively inexpensive, easy to handle, and offers sludge-free cleaning operation. Commercial activated charcoal has been popular for color removal by adsorption. The cost factor has been the major stumbling block for its use on an industrial scale. Hence, low-cost alternative adsorbents derived from industrial and agricultural wastes are becoming popular nowadays (Crini 2006, Gupta 2009, Ong et al. 2014, Antal et al. 2003). However, the efficiency of these wastes for

color removal is low, which can be improved by conversion of the selected lignocellulosic materials (Hassler 1967, Silva et al. 2001) and industrial as well as municipal wastes (Cazetta et al. 2016, Dias et al. 2015) into activated charcoal by the physical and chemical activation process. These processes reduce activated charcoal with a large surface area, which can attract various molecules in water on its surface (Hassler 1967). The nature of these attractive forces mainly depends on the size of the pores and the molecules attracted. These forces are called physical, or Van der Waal's forces and the adsorption involved is termed physical adsorption.

Sometimes in adsorption behavior, chemical change seems to be involved, which is called chemisorption. It is very specific and depends on the chemical nature of both adsorbate and adsorbent. Determining which kind of adsorption is predominant requires a lot of tests, physical and chemical, as well as the use of sophisticated instruments.

In our present study, we have used two biomasses, viz. areca nutshell, and coconut shell, to prepare activated charcoal with phosphoric acid as activating agent in the ratio phosphoric acid: biomass 3:1. Simple physical and chemical tests have been used to predict which kind of activated charcoal (AC) is effective for the color removal of entirely different kind of colored bodies from wastewaters. This has practical significance indeed. Few simple tests have been able to a priori predict or explain the uptake of natural plant-based dyes caramel (isolated from distillery spent wash) and a basic dye methylene blue from simulated wastewaters for the first time

MATERIALS AND METHODS

Precursor for Activated Charcoals (AC)

Dry areca nut shell samples were procured from coastal Karnataka, India. The fibrous portion of the shell was cut into small (10 mm × 10 mm) pieces and stored. Similarly, coconut shell was procured from a local dealer. It was crushed into small pieces of 10 mm size and stored

Preparation of AC

About 300 g of areca nut shell pieces were taken in a 2.0 L beaker. To this, about 627 cm³ of ortho-phosphoric acid [at H₃PO₄: Biomass:: 3:1, H₃PO₄ required is (300 × 3 × 1/(0.85 × 1.69)) = 627 cm³] dissolved in a small quantity of deionized water was added slowly along with deionized water, till the surface of the precursor was completely immersed in the acid solution. The mixture was kept soaked in the acid for 24 h with occasional stirring with a glass rod to improve the efficiency of the soaking of the biomass by the acid. After this

incipient wetting, the water content in the acid solution in the beaker was evaporated on a low flame. The dry mass in the beaker was transferred to a stainless steel (SS) container of size 30 cm × 9 cm × 9 cm. The SS container with acid-loaded biomass was placed in a muffle furnace with the lid partially open. A small flow of nitrogen gas was introduced into the furnace to maintain an oxygen-free atmosphere. The furnace was heated slowly to attain 400°C in 30 min and maintained at this temperature for 90 min. The heating was stopped immediately, and the material was allowed to cool under nitrogen flow. The cooled sample was removed from the furnace the next day to obtain acid-laden activated charcoal. This mass was washed several times with distilled water to remove the free phosphoric acid completely and then dried in an oven at 110°C for 6 h. The dried sample was crushed and sieved through a 100 mesh sieve to obtain areca nut shell activated charcoal (ASAC). Activated charcoal from coconut shell (CSAC) was prepared using a similar procedure. The results have been tabulated in Table 1.

Characterization

The characterization of both activated charcoal samples CSAC and ASAC was carried out to obtain the methylene blue, iodine, and specially devised acetic acid numbers.

Methylene blue number: The Methylene blue number of both CSAC and ASAC samples was determined as per the Indian Standard Specification IS 2230-1962 (Gokarn et al. 2005)

Iodine number: The iodine number of both CSAC and ASAC samples was determined according to D-4607-94 (Meshtram & Lataye 2014).

Acetic acid number: This novel concept was perceived and devised for the first time to quantitatively determine functional groups on activated charcoal surfaces (approximate). Grams of glacial acetic acid is adsorbed by 10 g of activated charcoal. The procedure consists of dissolving 50 cm³ of glacial acetic acid in water and making it up to a volume of 500 cm³ in a volumetric flask. Initially, blank reading is taken by titrating 10 cm³ of this solution against 1 N sodium hydroxide solution. One gram of activated charcoal sample is accurately weighed, mixed with 50 cm³ of the acetic acid solution in a 100 cm³ conical flask, and stirred slowly for 15 min using a magnetic stirrer. The solution is allowed to stand still for the active charcoal to settle. 10 cm³ of the supernatant solution is then titrated against 1 N sodium hydroxide solution. The amount in grams of acetic acid captured by 10 g of activated charcoal samples is calculated by material balance calculations. The acetic acid number of two activated charcoal samples, CSAC and ASAC, are tabulated in Table 1.

Table 1: Properties of activated charcoals.

	Areca nutshell (ASAC)	Coconutshell (CSAC)	Commercial E. Merck
Proximate Analysis:			
Moisture %	15.4	11.9	9.7
Ash %	6.5	4.9	4.9
Fixed carbon %	71.6	78.2	85.4*
Volatile matter %	6.5	5.0	
Physico-Chemical Properties:			
Surface area, m ² .g ⁻¹	1813	744	--
Iodine no.	906	901	--
Methylene blue no.	15	15	180
Acetic acid no.	3	6	--
Coloring Matter Adsorption/Removal Capacity, V_{C0} cm³/g			
Caramel	148.7	121.3	--
Methylene blue	514.0	--	--
Freundlich Constant (1/n)			
Caramel	1.1444	2.2939	
Methylene blue	0.4534	--	

Batch Adsorption Studies

Adsorbate Caramel

Almost pure caramel was isolated from distillery spent-wash procured from Ugar Sugar Works Ltd., Ugarkhurd, Karnataka, India. One liter of spent wash (COD29600) was mixed with equal water in a beaker. It was treated with inorganic coagulants to precipitate color bodies like melanoidin and lignin, which are bio-refractory and negatively charged. The treated sample was allowed for 12 h for the sludge to settle and subsequently filtered. The filtrate was treated with lime to precipitate excess coagulants and some coloring matter. This solution was again filtered to obtain a dark yellow-colored filtrate. A few drops of dilute hydrochloric acid were added to the filtrate to adjust the pH to 5. This is pure caramel solution in water and is pale yellow (Jagtoyen & Derbyshire 1991). The COD of this solution was 1280 ppm.

Adsorbate Methylene Blue

1.0 g of AR grade methylene blue sample was accurately weighed and dissolved in 1 liter of deionized water. The pH of the solution was found to be 5.3 and was used as such, without any pH adjustment, since the adsorption of methylene blue on activated charcoal is reported to be maximum at pH between 4 and 12 (Guo & Rockstraw 2006).

Adsorption Equilibrium Studies

Adsorption of Caramel on CSAC and ASAC

30 cm³ of caramel solution was stirred with 100 mg (m) of CSAC for 30 min using a magnetic stirrer. It was filtered,

and the optical density of the filtrate was measured using a UV-Vis spectrophotometer at 420 nm. The difference (x) in optical density (OD) of the original solution and filtrate measured the amount of caramel adsorbed by 100 mg of CSAC. Experiments were repeated with 100 mg increments of CSAC, and the corresponding OD was measured. The value of x/m corresponding to the OD was calculated. Preliminary studies indicated that 30 min of stirring was sufficient to reach equilibrium. Similar experiments were conducted using different weights of ASAC, and from the OD, the x/m was determined.

Adsorption of Methylene Blue on CSAC and ASAC

Adsorption experiments were conducted using 1000 ppm of solution of methylene blue as above with ASAC. The corresponding data with respect to OD and x/m were collected, as reported in the previous section. In this case, the time required to reach equilibrium was 60 min. However, when experiments were initiated using CSAC, the difference in OD after adsorption was negligible; this indicated that coconut shell-derived activated charcoal did not participate effectively in decolorizing methylene blue solution in the present case.

RESULTS AND DISCUSSION

Proximate Analysis and Yield of Activated Charcoals

The proximate analysis and yields of activated charcoals are presented in Table 1. Interestingly, the proximate

analysis of CSAC and ASAC are almost identical and closely resemble that of the commercially popular activated charcoal of E Merck (Personal communication, Merck Life Sciences Pvt. Ltd., 2017). It also justifies the experimental conditions selected for the preparation of activated charcoal. Sufficiently high ratio of impregnate to the precursor (phosphoric acid biomass:: 3: 1) in the present case coupled with the carbonization temperature of 400°C (90 min) must be responsible for obtaining good quality activated charcoal (Zuo et al. 1995). Another significant observation in the present study is that the nature and composition of precursors, particularly cellulose and lignin content (having measured values of 58%, 36% cellulose, and 16%, 48% lignin in areca nutshell and coconut shell, respectively) did not make much difference with respect to the composition of activated charcoal as revealed by the nearly identical values of proximate analysis parameters. It is reported that lignocellulosic materials undergo two processes during phosphoric acid activation: impregnation and heat treatment. During impregnation, phosphoric acid and lignocellulosic macromolecule composite is formed, and during subsequent heat treatment, modification of morphology and dimensions of cellular units existing before impregnation takes place (Molino et al. 1995, Savova et al. 2001, Tseng et al. 2003). Impregnated phosphorous is also responsible for the creation of a large number of micropores (Ying et al. 2006). The yields of active charcoal from areca nut shells and coconut shells were 27.7% and 22.1%, respectively. This yield value is higher than that of active charcoal obtained by one-step activation of biomass at 800°C (Savova et al. 2001).

Characterization of Activated Charcoals

Nature of Pores and Porous Surface

Activation of biomass produces activated charcoal, which comprises small holes and crevices providing a large surface area. These crevices are called pores, and pore size distribution depends on the biomass's nature and activation type. Depending on the incremental nature and size, these pores are classified as micropores (< 2 nm), mesopores (2-50 nm), and macropores (> 50 nm) (Boehm 1966). Iodine numbers that mainly characterize micropores contributing to the surface area were 906 mg.g⁻¹ and 901 mg.g⁻¹ for ASAC and CSAC, respectively. The measured surface area of the two activated charcoal samples, ASAC and CSAC, was 813 m².g⁻¹ and 744 m².g⁻¹, respectively. The high values of iodine numbers indicate the high surface area of activated charcoals, confirmed by surface area measurement (Table 1). The Methylene blue number of ASAC and CSAC were both 15 mg.g⁻¹, which is very low compared to the methylene blue number 180 mg.g⁻¹ of the commercial sample of E. Merck (Jagtoyen 1991). It is worth noting that the methylene blue

number signifies the number of mesopores in the activated charcoal (Leon et al. 1994). The role of mesopores will be discussed later.

Chemical Nature of the Porous Surface

Activated charcoal prepared in this study originates from the chemical activation of biomass using phosphoric acid. Hence, porous surfaces must necessarily be developed involving chemical functional groups. In most cases, the surface of the activated charcoals is known to possess oxygen functional groups, which are mainly acidic in nature. These are characterized by titration with an alkali called Boehm titration (Al-Degs et al. 2000). The acidic functional groups are responsible for the attraction of basic molecules leading to their chemisorption. In addition, basic groups are also developed on the carbon surface during its activation and/or further treatment with various chemicals and gas streams (Savova et al. 2000). Thus, activated charcoal can have on its surface both acidic and basic groups (Tseng et al. 2003, Al-Degs et al. 2000). Basic groups can also be estimated by Boehm titration using mild acids (Boehm 1966).

Simple Method for Characterizing the Nature of Chemical Functional Groups on Activated Charcoal

Activated charcoal contains many surface groups, such as carboxylic, lactonic, phenolic, carbonyl, and etheric (Leon et al. 1994). Determination of these groups by Boehm titration (Boehm 1966) involves using many chemicals and consuming more than 24 h (Li et al. 2009). The present method uses excess acetic acid to neutralize basic chemical functional groups on activated charcoal surfaces. On back titration of the unreacted acid, determination of the exact quantity of acetic acid adsorbed/absorbed by 10 g of activated charcoal is easily possible. It is named acetic acid number, and the details of the estimation of this number are already described in section 2.3.3. As seen in Table 1, the acetic acid number for ASAC was 3, while that for CSAC was 6. Its implication is discussed in the next section.

Adsorption of Coloring Matter on Two Activated Charcoal Samples

Following the adsorption equilibrium studies described in section 2.4.3, the nature of adsorption of coloring matter (caramel and methylene blue) by ASAC and CSAC was determined using Freundlich adsorption isotherm (Chermisnoff & Allerbusch 1983). This isotherm shows the distribution of adsorbate (coloring matter) between the adsorbent (activated charcoal) and solution phase at equilibrium. Empirical Freundlich equation, which relates the amount of adsorbate in the solution phase to that of adsorbent (activated charcoal) by the expression:

$$x/m = k C^{1/n} \quad \dots(1)$$

where x is the amount of adsorbate adsorbed, m is the weight of activated charcoal, C is the equilibrium concentration of adsorbate in solution after adsorption, and 1/n is the Freundlich constant, also called surface heterogeneity factor (dimensionless). Taking logarithm of both sides,

$$\ln(x/m) = \ln k + (1/n) \ln C \quad \dots(2)$$

A plot of ln(x/m) against ln C should yield a straight line from which x/m corresponding to the initial adsorbate concentration C₀ can be obtained. Here C corresponds

to the measured optical density or OD, as the change in OD has been directly proportional to the change in C in the concentration range studied. The adsorption capacity of activated charcoal can be estimated by using the relation:

$$V_{C_0} = (x/m)_{C_0} (V/C_0) \quad \dots(3)$$

V_{C₀} is the theoretical volume of colored solution (in cm³), which can be treated per gram of activated charcoal to completely remove the coloring body in the solution (or adsorption capacity).

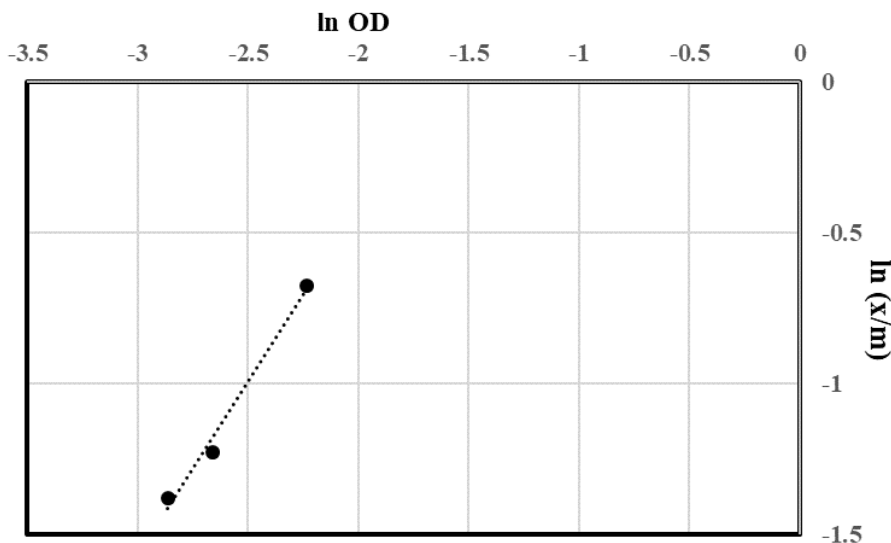


Fig. 1: Ln(x/m) versus ln OD plot for the adsorption of caramel (initial concentration of caramel: 1280 ppm, volume of caramel solution: 30 cm³, room temperature, pH: 5.0) on ASAC.

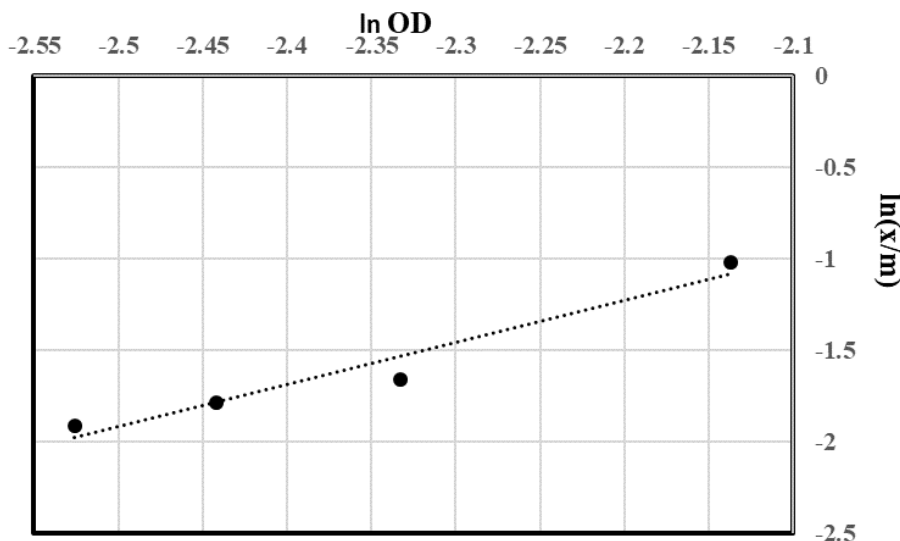


Fig. 2: Ln(x/m) versus ln OD plot for the adsorption of caramel (initial concentration of caramel: 1280 ppm, volume of caramel solution: 30 cm³, room temperature, pH: 5.0) on CSAC.

Adsorption of Caramel on ASAC and CSAC

The adsorption data of caramel on ASAC and CSAC (section 2.4.3.1) were used to obtain a plot of $\ln(x/m)$ against $\ln C_0$. These plots are presented in Fig. 1 (ASAC) and 2 (CSAC). Both the plots show straight lines indicating the applicability of Freundlich isotherm in both cases. The straight line plot was used to obtain values of $(x/m)_{C_0}$ and V_{C_0} for both the activated charcoal samples and are tabulated in Table 1. V_{C_0} or capacity of ASAC and CSAC for the capture of caramel was found to be $148.7 \text{ cm}^3 \cdot \text{g}^{-1}$ and $121.3 \text{ cm}^3 \cdot \text{g}^{-1}$ respectively. It is also quite evident that the capacity of activated charcoals in both cases was low. The value of constant $1/n$ of Figs 1 and 2 further confirms this fact. $1/n$ values were 1.1444 and 2.2939 for ASAC and CSAC, respectively. The value of $1/n$, greater than unity, also points to unfavorable adsorption for caramel on both ASAC and CSAC (Sogut & Caliskan 2017). Caramel, a sugar degradation product, is a high molecular weight compound. Caramel has a very small charge (Davis 2001). Hence it is clear that the adsorption of caramel on activated charcoals must be governed by physical adsorption. The mesopores formed during phosphoric acid activation are conducive to transport and adsorption on both ASAC and CSAC. The methylene blue numbers for ASAC and CSAC are similar and small, paving the way for similar capacity for the adsorption of caramel.

Adsorption of Methylene Blue on ASAC and CSAC

As seen in section 2.4.3.2, adsorption of methylene blue was possible only with respect to ASAC. The adsorption data of methylene blue was used to obtain a plot of x/m against

C_0 . The straight line plot shown in Fig. 3 again indicates the applicability of Freundlich isotherm in this case also. From the plot, $(x/m)_{C_0}$ was obtained, which was used to obtain the value of V_{C_0} , the capacity of ASAC as $514 \text{ cm}^3 \cdot \text{g}^{-1}$. The slope of the Freundlich isotherm plot, $1/n$, has a value of 0.4539, indicating highly favorable methylene blue adsorption on ASAC (Sogut & Caliskan 2017). Methylene blue is known to be a basic dye (Meshtram & Lataye 2014), and the Coulombic attraction between its positively charged ions and the negative surface of activated charcoal (ASAC) seems to be responsible for their efficient binding. Our studies on acetic acid numbers have indicated that ASAC has a lower value of the acetic acid number of 3 than 6 for CSAC. This confirms that ASAC has more acidic groups than CSAC, and CSAC must have a good number of basic groups on its surface, as indicated by a higher acetic acid number. The highly basic nature of CSAC is the reason for its negligible affinity for the basic dye methylene blue, as seen in section 2.4.3.2.

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CONCLUSIONS

Two types of activated charcoals were prepared using areca nutshell and coconut shell by chemical activation. The

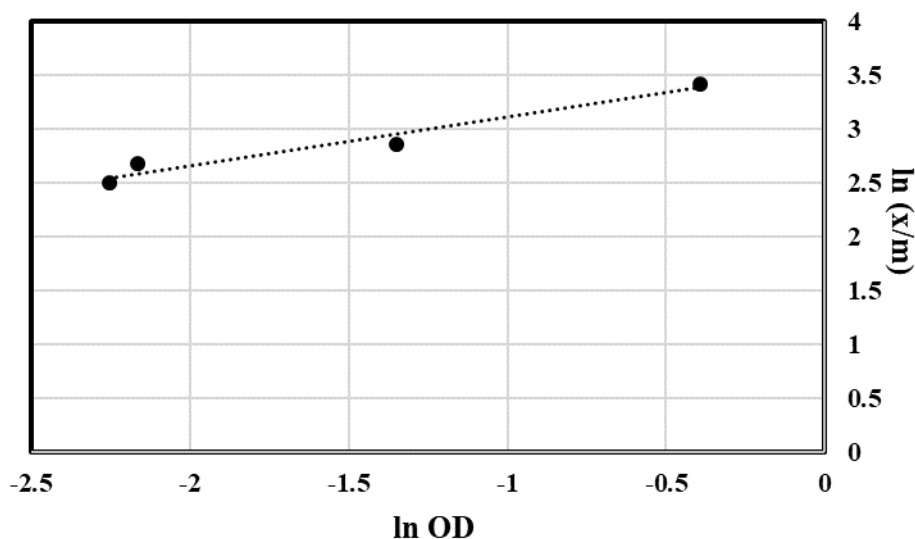


Fig. 3: $\ln(x/m)$ versus $\ln OD$ plot for the adsorption of methylene blue (initial concentration of methylene blue: 1000 ppm, volume of methylene blue solution: 30 cm^3 , room temperature, pH: 5.3) on ASAC.

preparation conditions have proven conducive to obtaining good quality active charcoals with highly developed pore structures. The proximate analysis parameters of these samples were comparable to those of commercial activated charcoal of E. Merck. The adsorption data of caramel solution on ASAC and CSAC and that of methylene blue solution on ASAC fitted well with Freundlich isotherm. The acetic acid number of activated charcoal, devised and estimated for the first time, could explain the surface groups' basic/acidic nature, influencing the adsorption/absorption of chemically charged coloring matter.

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