

Adsorption of VOC on steam activated carbon derived from coconut shell charcoal

S Anuradha^{1,2}, K Joseph Antony Raj², T Elangovan² & B Viswanathan^{2*}

¹Department of Chemistry, PSNA College of Engineering and Technology, Kothandaraman Nagar, Dindigul 624 622, India

²National Centre for Catalysis Research, Indian Institute of Technology Madras, Chennai 600 036, India

Email: bvnathan@iitm.ac.in

Received 16 December 2013; accepted 25 April 2014

The activated carbon AC1, AC2 and AC3 are produced from the coconut shell charcoal with different levels of activation by steam and temperatures of 800°C, 850°C and 900°C. The AC3 activated at 900°C show about 50 m²/g of higher surface area than AC1 and AC2 which are activated at 800°C and 850°C, respectively. The maximum BET surface area and iodine sorption on AC3 are found to be 1262 m²/g and 1194 mg/g respectively. Adsorption capacity of all the three activated carbon has been examined with volatile organic pollutants, carbon tetrachloride, benzene, ether and *n*-pentane. The order of adsorption is CTC > benzene > ether > *n*-pentane. An empirical relationship between VOC and iodine number is obtained for the activated carbon samples. This clearly shows that the adsorption capacity depends on the attractive forces between the AC and nature of pollutant. Kinetic data reveals the uniform distribution of pores in all the activated carbon irrespective of the activation temperature.

Keywords: Activated carbon, VOC, Coconut shell charcoal, Kinetic study, Steam activation

The emission of volatile organic compounds (VOC) has harmful effects on environment. Diverse methodologies have been developed to restrain the VOC emission, and one of the most important techniques employed involves adsorption onto porous adsorbents. There are a number of commercially available adsorbents including activated carbon fiber (ACF), alumina, silica gel and zeolites. The class of activated carbon (AC) adsorbents proves to be promising owing to their high adsorption capacity and regenerability. AC derives its capacity from their high surface area, pore size distribution, surface functional groups, and polarity¹⁻³. Interestingly, AC can be prepared from diverse sources such as coconut shell, wood, bone and jute stick char.

AC has been shown to be effective in the removal of aromatic hydrocarbons⁴⁻¹¹. The adsorption and desorption dynamics of aliphatic hydrocarbon such as pentane and oxides of carbon and sulfur onto AC has been studied in detail¹². In the adsorption of benzene from both gaseous and aqueous phases, pore-blocking effect plays a major role which strongly depends on the polarity of the carbon surface¹³. A change in the pH has been shown to alter benzene adsorption¹⁴. A lower content of oxygenated acidic surface groups also contributes to better adsorption capacity¹⁵.

Catalytic and heterogeneous adsorption behavior of Benzene, Toluene and Xylene (BTX) has been studied employing sulfuric acid treated Pt/AC catalyst¹⁶. Ozonation of AC increases the surface area by increasing the microporosity and functional groups which also increases the adsorption of benzene¹⁷. Jinjun *et al.* reported that in case of multi-walled nano tubes (MWNT), the adsorption of benzene is important when compared to the conventional AC¹⁸. Single-walled carbon nano tubes (SWCNT) are efficient benzene and toluene adsorbents and find use in water and waste water treatment¹⁹. In this investigation, we report the preparation of AC by steam activation of coconut shell and adsorption behavior of the AC towards benzene, *n*-pentane, carbon tetrachloride and ether. In addition, attempts have been made to monitor the kinetics of adsorption.

Experimental Section

The various chemicals employed in this study were of analytical grade and were procured from Qualigens. The coconut shell charcoal of 3 to 5" size, with moisture content of 12%, volatile content of 17% and fixed carbon of 80% was used in this investigation. The activation of charcoal was effected

in an atmosphere of steam in a vertical tubular furnace. Steam is injected at a pressure of 1.5 kg/cm². The activated carbon samples were prepared at temperatures of 800°C, 850°C and 900°C, and the samples are abbreviated as AC1, AC2 and AC3, respectively. Each of the samples was sieved to generate particles of mesh size 8, 12, 16, 40, 60, 80 and 100. The reported particle size, in terms of mesh, is within $\pm 5\%$.

The iodine number for the activated carbon samples was measured iodimetrically. The samples were ground well, sieved through a 325-mesh and dried at 105°C prior to the measurement. Care was taken to remove any sulfur present in the sample by boiling gently. The BET surface area of the activated carbon samples prepared in this study was measured on Micromeritics ASAP2020 surface area and porosity analyzer after the samples were degassed in vacuum at 300°C for 3 h. BET surface area was calculated from the BET plot.

The experiments of adsorption of organic pollutants were carried out at ambient temperatures of 25-28°C. A typical procedure employed is outlined below. A known amount (15 g) of dried AC sample was taken in a pre-weighed U-tube, and air laden with organic pollutant was passed through the tube at 1670 mL/min. Initially the adsorption was carried out for 30 min and at the end of this period the tube was weighed. Thereafter, the tube was weighed at 5 min. interval until a constant weight was observed. The adsorption capacity of the AC samples was calculated from the increase in weight of the tube. The percent adsorption of various pollutants under investigation was determined by the following equation:

$$\text{Amount adsorbed in wt.}\% = \left(\frac{\text{the amount of pollutant adsorbed}}{\text{the amount of activated carbon}} \right) \times 100$$

Results and Discussion

Charcoal has very limited adsorption capacity as the pore structure is blocked as such and has to necessarily be activated. The activation of charcoal may be achieved by steam activation or chemical activation process. The former process has been employed in this investigation. During steam activation, steam reforming reaction, formation of carbon monoxide and hydrogen occurs. The steam activation process carbonizes the charcoal substantially resulting in a porous structure. The recovery of AC after the burn off by steam was

at 40-43% which is comparable with literature²⁰. The ash and moisture content of the AC samples were found to be in the range 0.3-0.5% and 1.3-1.7%, respectively.

The Iodine number and BET-surface area were measured for the AC samples and the results are given graphically in Fig. 1 and Fig. 2. Activation temperature increases the porosity and is well reflected in the iodine number. An inspection of the data reveals that both iodine number and BET-surface area, which are important measures of adsorption capacity, increases with the temperature of the activation process in addition to the mesh size of AC mesh size. A steep increase in trend of iodine number is observed when the activated carbon size decreased from 8 to 12 and thereafter a

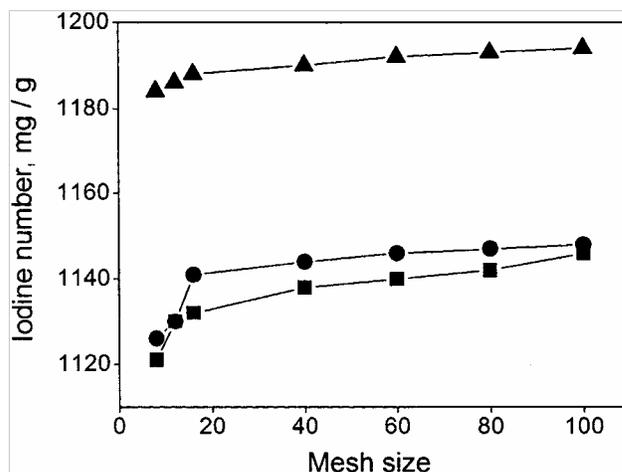


Fig. 1—Effect of mesh size of activated carbon on iodine number (■ AC1, ● AC2, ▲ AC3)

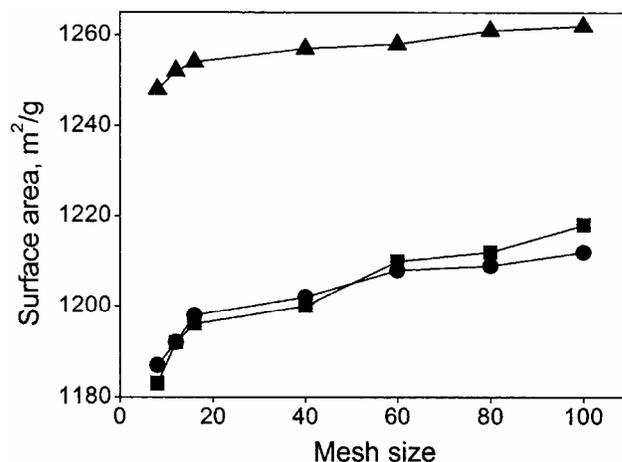


Fig. 2—Effect of mesh size of activated carbon on surface area (■ AC1, ● AC2, ▲ AC3)

plateau was observed. This trend clearly suggests that decreasing size of activated carbon by milling does not always increase the adsorption capacity as there seems to be a limit for enhancement in surface area with decreasing size. Similarly, BET-surface area also shows increasing trend with decreasing mesh sizes from 8 to 12 and thereafter approaches the limiting value. The increase is found to be higher for AC3 and follows the order $AC1 > AC2 > AC3$. In other words, increase in surface area is not significant at lower particle sizes. Interestingly, AC3, the activated carbon prepared at 900°C is found to possess a higher BET-surface area and iodine number than AC1 and AC2. Both AC1 and AC2 have more or less similar BET-surface area and iodine number.

The organic pollutants employed in the study, viz., benzene, *n*-pentane, carbon tetrachloride and ether fall in the category of VOC due to their high volatile nature. They encompass hydrocarbons (aliphatic and aromatic), oxygenates and chlorinated organics which are usually found in industrial and motor vehicle emissions. The adsorption of the VOC expressed as percentage of AC used is shown in Figures. 3a, 3b and 3c. It is apparent from the data that for all the three AC samples of various mesh sizes, the adsorption capacity follows the order $AC3 > AC2 > AC1$ and adsorption order is found to be $\text{CCl}_4 > \text{benzene} > \text{ether} > n\text{-pentane}$ (Figures. 3a, 3b and 3c). The increase in adsorption of CCl_4 , ether and *n*-pentane with mesh size of AC is 3 wt.% or less. On the other hand, the increase is in the range of 3.9-6 wt.% in case of benzene. An interesting observation is that the lowest adsorption of AC2 is greater than the highest adsorption observed for AC1, and the lowest adsorption of AC3 is greater than the highest adsorption observed for AC2. The AC3 of mesh size 100 exhibits the greatest adsorption for all the organic pollutants. It may be noted that carbon tetrachloride adsorption equivalence per every gram of *n*-pentane, ether, and benzene are 2.1 g, 1.65 g and 1.55 g, respectively.

There seems to be an empirical relationship between the adsorption behavior of the pollutants and the iodine number of the AC samples. It is obvious that *n*-pentane does not show much affinity for adsorption by virtue of their chemical nature. On the other hand, the other pollutants seem to interact with AC electronically. The carbon

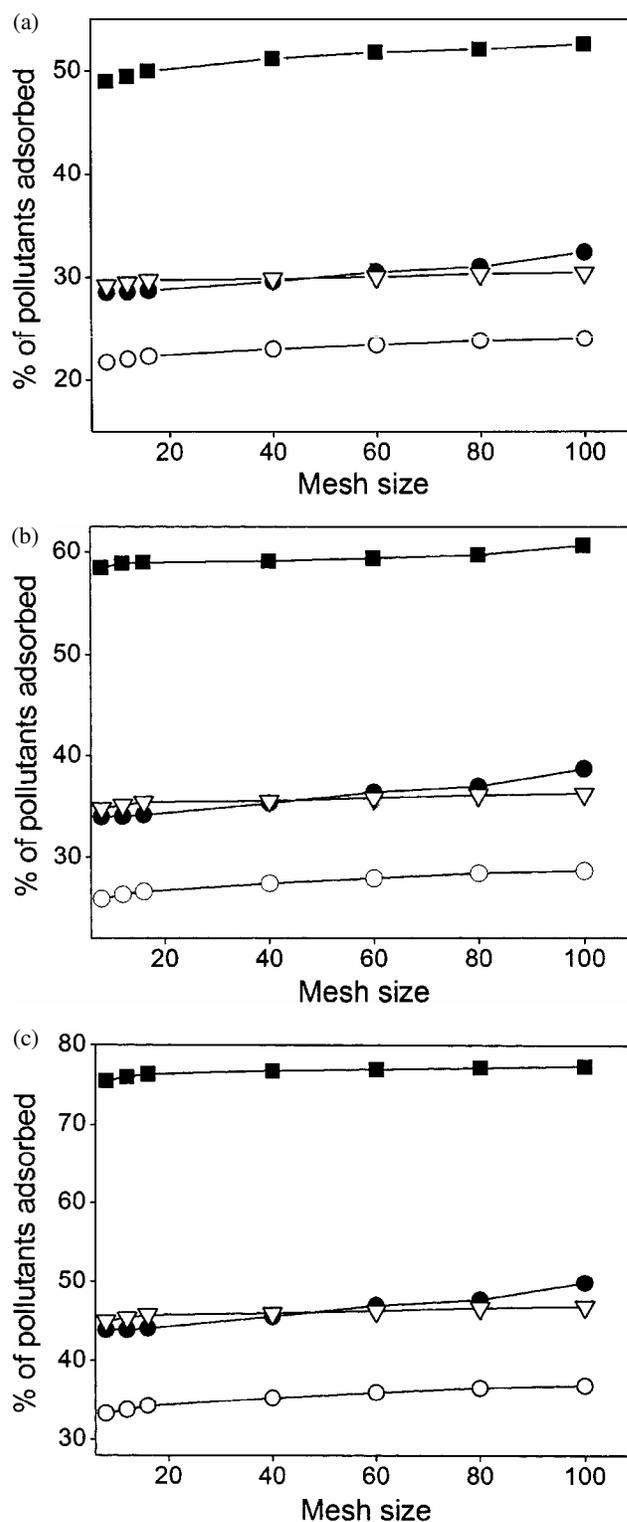


Fig. 3(a-c)—Effect of mesh size of activated carbon (a) AC1 on adsorption of pollutants (■ CCl_4 , ● benzene, ▽ ether, ○ *n*-pentane); (b) AC2 on adsorption of pollutants (■ CCl_4 , ● benzene, ▽ ether, ○ *n*-pentane) and (c) AC3 on adsorption of pollutants (■ CCl_4 , ● benzene, ▽ ether, ○ *n*-pentane)

atom of AC may donate its $2p$ electrons into the partially filled p orbitals of oxygen atom of ether and chlorine atom of carbon tetrachloride. It is likely that the interaction of carbon with benzene may involve π electron cloud of the latter.

The kinetics of adsorption of the pollutants on the three AC samples has been followed for 30 min. The adsorption attained equilibrium in about 30 min. The adsorption of VOC beyond 30 min. was not found to alter the equilibrium state. Plot of amount of CCl_4 adsorbed against time was constructed and shown in Fig. 4. It is observed that the uptake of the pollutants was rapid in the initial 20 min. and thereafter tends to be slow and finally approaches the saturation. The order of uptake of VOC is found to be $\text{AC3} > \text{AC2} > \text{AC1}$ which parallels with the surface area of the respective AC. It was observed that the adsorption of pollutants proceeded linearly in the initial 15 min. and the adsorption could be analyzed

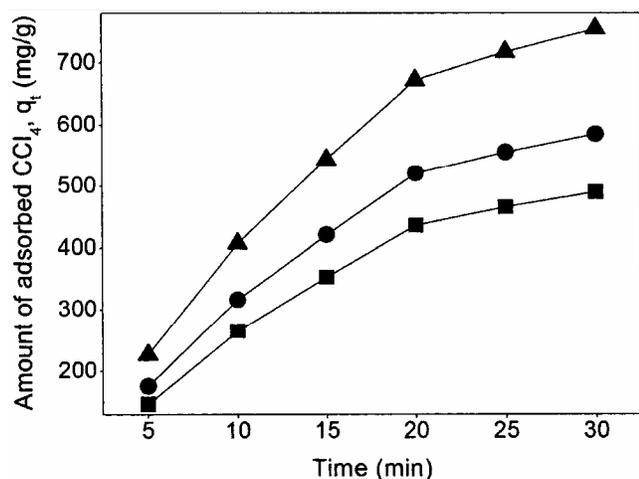


Fig. 4—The adsorption of CCl_4 with time over various activated carbon (■ AC1, ● AC2, ▲ AC3)

using pseudo-first order kinetic equation which is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

where, q_e and q_t (mg/g) are the amount of adsorbate at equilibrium and at time t (min), respectively. k_1 (min^{-1}) is the first-order rate constant. The pseudo-first order rate constant ($k_1 = -\text{slope}$) was calculated by plotting $\ln(q_e - q_t)$ against time. The plot of pseudo-first-order kinetics of CCl_4 over the three ACs is shown in Fig. 5, and the rate constants of all VOC studied is displayed in Table 1. It shows that the rate of adsorption of the VOC is similar in all the AC studied. It clearly indicates that the distribution of pores is similar in all the AC; however the amount of VOC adsorption increases from AC1 to AC3. The entire adsorption data could not be treated successfully employing second order kinetic equation.

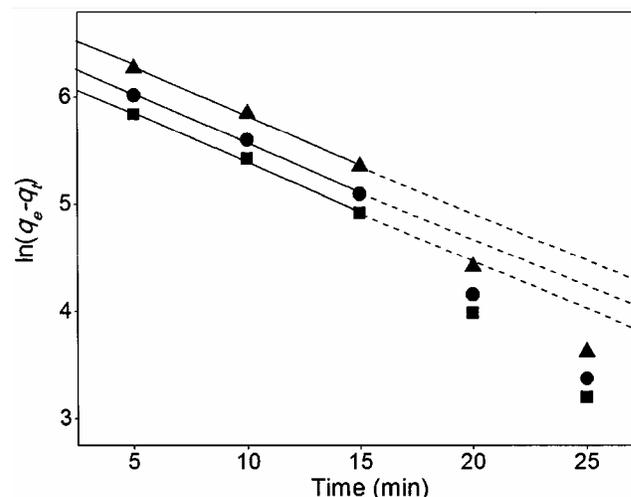


Fig. 5—Plot of pseudo-first order kinetics for the adsorption of CCl_4 on various activated carbon (■ AC1, ● AC2, ▲ AC3)

Table 1—Pseudo-first order rate constant, intercept and R^2 for the adsorption of CCl_4 , benzene, n -pentane and ether over various AC

Adsorbent	Kinetic data (graph)	CCl_4	Benzene	n -Pentane	Ether
AC1	k_1 (min^{-1})	0.092 ± 0.005	0.092 ± 0.005	0.080 ± 0.002	0.092 ± 0.004
	Intercept	6.310 ± 0.050	5.773 ± 0.049	5.347 ± 0.025	5.790 ± 0.049
	R^2	0.995	0.995	0.998	0.995
AC2	k_1 (min^{-1})	0.092 ± 0.003	0.091 ± 0.004	$0.085 \pm 5.7 \times 10^{-4}$	0.091 ± 0.005
	Intercept	6.490 ± 0.050	5.937 ± 0.044	5.593 ± 0.006	5.96 ± 0.056
	R^2	0.995	0.996	0.999	0.994
AC3	k_1 (min^{-1})	0.092 ± 0.005	0.092 ± 0.005	$0.085 \pm 5.7 \times 10^{-4}$	0.091 ± 0.004
	Intercept	6.740 ± 0.050	6.203 ± 0.049	5.843 ± 0.025	6.216 ± 0.044
	R^2	0.995	0.995	0.999	0.996

Conclusion

Coconut shell based activated carbon is prepared by steam activation using rotary kiln and thereafter 4 × 8 mesh size of activated carbon is ball milled and sieved to prepare different mesh size (8, 12, 16, 40, 60, 80 and 100) of activated carbon. The activation conditions such as activation temperature and steam flow determines the surface area. The bulk density, Iodine number and BET-surface area of the activated carbon are found to increase with temperature of activation. The AC3 activated at 900°C show about 50 m²/g of higher BET-surface area than the AC1 and AC2 activated at 800°C and 850°C, respectively. Adsorption capacity of AC for CCl₄, benzene, *n*-pentane, and ether is found to increase with increasing iodine number and decreasing particle size. This trend is attributed to the increasing surface area of the activated carbon. Decrease in mesh size does not have influence in adsorption of non polar pollutants. The pseudo-first order kinetic model shows that the adsorption of VOC on the steam activated carbon is independent of the temperature of activation.

Acknowledgement

The authors acknowledge the Department of Science and Technology, Government of India for funding the National Centre for Catalysis Research (NCCR) at IIT-Madras.

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