



## Effect of temperature and surface area on adsorption of chlorine on different adsorbent carbons

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**Abstract:** Chlorine is used in several ways in industry. In such situations, where residual chlorine persists as pollutant, Activated carbons like animal charcoal, carbon black and coconut charcoal can serve as agents to remove residual pollutant "chlorine" by the process of adsorption. Five samples of Carbon black, six samples of active Carbons and two samples of charcoals were treated with a stream of chlorine @0.4 litre/hour at temperature varying from 30° to 120° C. Chlorine is adsorbed partially physically and partially chemically. Percentage of the chemisorbed increases with rise in the temperature. Maximum percentages of chemisorptions occur at 120° C while the maximum uptake, physical as well as chemical, takes place at 30° C, which was the lowest temperature. It is seen that activated carbon, carbon blacks and charcoal differ markedly by in their total chlorine uptake at 30° C. Activated carbons associated with high surface were seen to take up maximum chlorine. Fall in surface area is more in active carbons as compared to carbon black due to greater adsorption of chlorine. This probably shows that micro porous carbons are better adsorbent for chlorine adsorption. The unsaturated sites also play far dominant role and provide centres where the adsorption takes place predominantly. Uptake of chlorine is enhanced on evacuating the carbon samples at 600° C and 1000° C. This is due to the creation of more unsaturated sites. Process of adsorption cum chemisorption takes place through different kinetic stages with different energetics. The activation energies keep on increasing with increasing amounts of chemisorption.

**Keywords:** Activated carbons, Adsorption, Carbon blacks, Charcoal

### INTRODUCTION

Studies concerning adsorption of gases like Chlorine, Bromine and Iodine on adsorbent carbons have got immense practical utility in industrial set ups where these halogens are manufactured on commercial basis or are used as means to achieve some other commercial targets. In such circumstances there is a need to evolve adsorbent carbons which would serve as the best adsorbents Chlorine, bromine and Iodine as the case may be.

Earlier workers (Barton *et al.*, 1968, Koltsov *et al.* (1973), Puri *et al.*, 1963, 1966, 1972, 1978a,b; Puri and Bansal, 1966, Puri and Seghal, 1967, Hall and Holmes, 1992) have worked on Iodine and other Halogens. However, only very limited information is available on chlorine its adsorption by various carbons and hence the present studies. Others who have worked in this area adsorption are Kisliuk (1957), Tabias and Soffer (1985a,b), Taylor *et al.* (1991), Tieglitz *et al.* (1991), Brandt *et al.* (1993), Rozanow and Krylov (1997), Uner *et al.* (1997), Narayan and King (1998), Sidhu *et al.* (1995), Uner (1998), Dellinger and Taylor (1998), Vanderwiel *et al.* (1999), Xhrouet *et al.* (2001), Zupanc *et al.* (2002), Wilson *et al.* (2005), Barnes *et al.* (2009), Sivaraman *et al.*, 2009, Trens *et al.* (2009), Ferrari *et al.* (2010), Scopelliti *et al.* (2010) and Pilatowsky

*et al.* (2011). In the present study, an attempt has been made to determine the adsorbing capacities of different samples of carbon in respect of Chlorine.

### MATERIALS AND METHODS

Six samples of commercial available activated Carbons, five samples of Carbon black, sugar coconut-shell Charcoal have been used in the present investigation. Active carbons have been designated as A B G H J. Carbon blacks, including Graph on used in some of the experiments were received from United States. Sugar and Coconut-shell charcoal used in the present investigation were prepared by the carbonization of recrystallized cane sugar or coconut-shells.

In order to modify surface characteristics of the above original sample of carbons, they were given subsequent treatment as follow:

Carbons were out-gassed in a resistance tube furnace, the temperature of which could be controlled with the help of variance transformer.

In order to prepare carbon with different burn offs, the sample were evacuated at 625° C and then at 800° C to remove the suitable oxygen complexes. Treatment with Potassium persulphate is done by a mixing a carbon sample (1 portion) with 200 ml of nearly saturated solution

of Potassium persulphate in  $2\text{H}_2\text{SO}_4$ .

Treatment with hydrogen peroxide is done by mixing carbon sample (1 gm portion) with 100 ml of 3N hydrogen peroxide and the suspension shaken for 24 hour. The carbon was filtered, washed and dried in air oven at  $120^\circ\text{C}$ . Adsorption of chlorine was studied in flow system. The progress of reaction was followed by noting the weight of chlorine adsorbed on the carbon using simple Mc-Bain Sorption balance technique (Mc Bain, 1932).

## RESULTS AND DISCUSSION

The preliminary experiment showed that maximum adsorption of chlorine takes place when 0.3gm of carbon sample is used. It is seen that maximum chlorine uptake occurs at  $30^\circ\text{C}$  and with further increase of temperature it decreased progressively. It is also seen that chlorine is being adsorbed physically as well as chemically. Puri and Bansal (1966) have found similar trends on bromine. After studying the influence of surface area on adsorption behavior of carbon, it is seen that activated carbons, carbon black and charcoal differ markedly in their total chlorine uptake at  $30^\circ\text{C}$ . Activated carbons associated with high surface area are seen to take up maximum chlorine. Puri and Sehgal (1967) have found similar carbon halogen surface complexes.

The stability of chemisorbed chlorine was tested next in the case of each carbon by evacuation of the sample on which chlorine was allowed to be chemisorbed at temperature ranging from  $30$  to  $100^\circ\text{C}$ . The data are presented in Table 1.

In order to get some further insight, carbon blacks and charcoals were used after out-gassing either at  $600$  or  $1000^\circ\text{C}$  or both. Active carbons which are already heated to sufficiently high temperature during their preparation were not used for similar investigation. With increase in surface area on out-gassing the chlorine uptake is enhanced considerably. Barton *et al.* (1987) has observed similar trends while studying the effect of chlorination on the adsorption properties of water on carbon cloth. This may be due to generation of additional unsaturated sites. Walker and Kini (1965) have shown that certain active sites are generated in graphitized carbon blacks on bringing about of their burn offs in oxygen at  $625^\circ\text{C}$  at very low pressure.

Presence of oxygen complexes inhibits chlorine adsorption on carbons. These oxidized carbon samples were out-gassed at  $1000^\circ\text{C}$ , which has been shown to result in creation of new unsaturated sites. The surface concentration unsaturated sites was determined by estimating bromine value. It was also interesting to estimate surface area of carbon after chlorine uptake. In all carbon surface area is seen to fall considerably on sorption of chlorine. Fall in surface area is more in active carbon as compared carbon black due to greater sorption

of chlorine shows that micro porous carbons are better adsorbent for chlorine adsorption. Brandt *et al.* (1993) have worked surface area concept in reference of Co adsorbed on  $\text{Pt/SiO}_2$  of the different particle size distributions.

The kinetics of chlorine sorption on carbons can be represented by Elovich equation stated as:

$$dq/dt = ae^{-aq} \quad (1)$$

where  $q$  is the amount adsorbed at time  $t$  and ' $a$ ' and ' $a'$ ' are constants. ' $a$ ' represents the initial rate. The integrated form of the equation may be written as:

$$q = 2.303 / \log(1+at) \quad (2)$$

and constant ' $a$ ' can be determined from the slope of the plots between  $q$  and  $\log t$  where as the rate constant ' $a$ ' can be evaluated from equation (2) on substituting the value of ' $a$ '. Elovich plot for sorption of chlorine on carbon ' $a$ ' at different temperature and atmospheric pressure shows that each linear region correspond to sorption at discrete types of sites it appear that at temperature upto  $85^\circ\text{C}$  three different types of sites are involved in the sorption process. However, the number reduces two at  $120^\circ\text{C}$ .

The reduction in these types of sites involved at  $120^\circ\text{C}$  may be due to greater amount of chlorine being chemisorbed. All the data points can grouped into 3 different linear regions showing that the sorption of chlorine on carbon surfaces occur in a discontinuous manner, each of the three linear regions corresponds to sorption on three different types of site. Further studies shows that only two types of sites are involved during sorption at  $120^\circ\text{C}$ , where as sorption at lower temperature involve three types of sites that exist on carbon surface. The late parameter's ' $a$ ' and ' $a'$ ' of the Elovich equation for each sorption region at different temperature in Table 2. It observed that ' $a$ ' and ' $a'$ ' are different for different regions. The value is also seen to be influenced by temperature of the reaction.

The value of activation energy for the various kinetic stages as calculated from the rate data are given in Table 3. These are seen to vary from 3.750 to 7.920 kcal/mgl. It appears that chlorine is held physically during the first kinetic stage and it dissociate feeding to chemisorptions during the II and III kinetic stages. Thus it is predicted that at lower temperature physical adsorption takes phase and at higher temperature in at  $120^\circ\text{C}$ . The Chemisorptions takes phase. To remove chlorine pollutant the temperature maintained must be between  $100^\circ\text{C}$  to  $120^\circ\text{C}$ . Above  $120^\circ\text{C}$  desorption of chlorine will start.

Precisely speaking, at ambient temperatures, total uptake of pollutant chlorine is maximum. But at higher temperatures the retained amount of pollutant chlorine is maximum. Hence, activated animal charcoal, carbon black and boconut charcoal can be used to remove, pollutant chlorine. Residual chlorine in various industrial

**Table 1.** Effect of temperature on chlorine uptake by carbon 'A'.

Temperature (°C)	Total Chlorine uptake (mg/g)	Amount of Chlorine physically adsorbed (mg/g)	Amount of chlorine chemisorbed i.e. amount retained on evacuation (mg/g)	Percentage of chlorine chemisorbed
30	745	352	393	52.7
70	540	219	321	59.4
85	425	150	275	64.7
120	395	105	290	73.4

**Table 2.** Parameters in the Elovich equation for sorption of chlorine on active carbon 'A' at different temperatures and stages.

Temperature (°C)	Stages					
	I		II		III	
	a*		a		a	
30	30.92	.057	118.05	0.0152	212.32	0.0022
70	5.39	.016	29.36	0.0094	158.726	0.0022
85	11.89	.115	37.950	0.0085	109.37	0.0036
120	47.401	0.143	58.066	0.00525	-	-

**Table 3.** Activation energy for various stages involved during sorption of chlorine on Active-Carbon 'A' at atmospheric pressure.

Stage	Activation energy (Kcal-mg <sup>-1</sup> )
I	3.750
II	4.554
III	7.920

operations is a cause of concern for its removal. It can be better removed. It can be better removed by adsorbent carbons. The adsorption process is regulated by surface area of adsorbing carbons and temperature regimes. In the present studies five samples of carbon, six samples of actual carbons and two samples of Charcoal have been considered for experiments. Temperature regime varies between 30°C to 120°C. It is seen that Chlorine is partially absorbed in a chemical action and partially physically. It has also been observed that maximum absorption of chlorine takes place at 120°C. Microporous carbons are better adsorbents.

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