

## ADSORPTIVE REMOVAL OF COBALT FROM AQUEOUS SOLUTION BY ACTIVATED CARBONS

DIKSHA AGGARWAL AND MEENAKSHI GOYAL

Department of Chemical Engineering and Technology  
Panjab University, Chandigarh 160 014, India

**Key words :** Activated carbon, Chemically modified carbons, Activation oxidation.

### ABSTRACT

Adsorption of Co(II) ions from aqueous solutions using two samples of activated carbon fibers and two samples of granulated activated carbons has been studied. The adsorption isotherms obey Freundlich isotherm equation. The linear Freundlich adsorption isotherms have been used to calculate  $X_m$  and  $n$ . The adsorption does not depend on the surface area but is strongly influenced by the presence of carbon-oxygen groups on the carbon surface. The amounts of these surface groups was enhanced by oxidation of the carbons with nitric acid and oxygen gas and decreased by degassing of the oxidized samples at 400, 650 and 950°C. The adsorption of Co(II) ions increased on oxidation and decreased on degassing. The increase in adsorption was much larger when the oxidation was carried out with nitric acid. This treatment incidentally results in a larger increase in the amounts of the oxygen surface groups compared to oxidation with oxygen gas. The decrease in adsorption on degassing depends on the temperature of degassing, being larger on degassing at 650°C than on degassing at 400°C. The increase in adsorption on oxidation and the decrease in adsorption on degassing have been attributed to an increase in the concentration of acidic groups on the carbon surface on oxidation and their decrease on degassing. The presence of acidic carbon-oxygen groups on the carbon surface and their ionization in aqueous solution also changes the pH of the carbon suspension. The effect of solution pH on

**the adsorption has also been studied and suitable mechanisms involved in the adsorption of Co(II) ions on activated carbons from solutions have been discussed.**

## INTRODUCTION

The adsorption of inorganic metal ions from aqueous solutions has several aspects: the recovery of precious metals like gold and silver, the loading of activated carbons with certain metals to produce impregnated carbons and the removal of heavy metal pollutants from drinking water. Cobalt is one such heavy metal which is present in the waste water from several industries and is toxic to human beings when taken even in small quantities. Consequently its removal by adsorption using different types of activated carbons has been the subject matter of several investigations.

Kaya and Akyol (1992) studied the adsorption of Co(II) ions from aqueous solutions by activated bentonite as a function of contact time, temperature and concentration of the solution and found that appreciable amounts of the metal were adsorbed. Netzer and Hughes (1984) examined the influence of solution pH on the adsorption of Co(II) ions on a number of activated carbons and observed that the adsorption depended on the pH of the solution and showed a maximum at pH 4. Paajanon *et al.* (1997) reported the adsorptive removal of traces of radioactive cobalt (Cobalt 60) from nuclear waste solutions at different pH values using activated carbons prepared from peat, coconut shell and coal while Tekker *et al.* (1977) used activated carbons obtained from rice hulls to study the effect of solution pH and concentration, contact time and temperature on the removal of Co(II) ions from waste water. The results showed an increase in adsorption with increasing pH of the solution, the optimum pH being 6-7. These workers suggested that the adsorption probably involved an ion-exchange mechanism. Shakir *et al.* (1993) also studied the adsorption of cobalt ions from radioactive process waste water on an activated charcoal in the presence of gelatin as a collector and observed that more than 90% of the cobalt could be removed. The results were discussed in terms of the hydrolysis of the metal ions. In a subsequent publication (1993), these workers observed that while the adsorption of Co(II) ions decreased in the presence of strongly ionized cationic or anionic surfactants it was enhanced in the presence of weakly ionized surfactants. Takiyama and Huang (1997) also studied the influences of pH on the adsorption of Co(II) ions on acidic and basic activated carbons and observed a sharp increase in adsorption in the pH range 2-6 for acidic carbons and in the pH range 6-9 for basic carbons. Kim *et al.* (2002) investigated the electrosorption of Co(II) ions on a cellulose based activated carbon fibre KF-1500 after modifying the ACF surface by dipping in nitric acid and sodium hydroxide solutions at room temperature. The electrosorption capacity of the ACF increased on treatment both with HNO<sub>3</sub> and NaOH. Rivera-Utrilla *et al.* (1987) studied the adsorption of Co(II) from aqueous solutions on a series of activated carbons obtained from almond shell. The adsorption was found to increase with the degree of activation as

well as by the oxidation of the carbon surface indicating that both the nature and the porosity of the carbon surface determined the uptake of Co (II) ions. These workers also studied the influence of pH on the adsorption of Co (II) ions.

It appears from the above perusal of the literature that the influence of nature of carbon surface and the type of carbon-oxygen surface groups on the adsorption of Co(II) ions by activated carbons from aqueous solutions and the mechanisms involved have not been examined. The present work was undertaken with these aspects in mind.

## Experimental

Two samples of granulated activated carbons (GAC-K and GAC-S) obtained from Norit N.V. Netherlands and two samples of activated carbon fibres (ACF-307 and ACF-310) obtained from Ashland Petroleum Company, Kentucky, U.S.A. have been used as adsorbents. The granulated carbons are peat based materials activated with steam while the activated carbon fibres are pitch based materials. The activated carbons have been oxidized with nitric acid in the liquid phase and with oxygen gas at 350°C to enhance the amount of carbon-oxygen surface groups (Bansal *et al.* 1978, Goyal *et al.* 1999, 2001). The oxidized activated carbons were then degassed at 400, 650 and 950°C to gradually eliminate varying amounts of these carbon-oxygen surface groups (Goyal *et al.* 2001, Bansal *et al.* 1978, Puri and Bansal 1964). The procedure for oxidation and degassing have been described elsewhere (Bansal *et al.* 1978, 1964) but brief descriptions are given below.

### Oxidation with nitric acid

The activated carbon sample (5g) was heated with 150 mL of 50 % nitric acid in a borosil beaker of 250-mL capacity in a water bath maintained at about 80°C. When all but about 10 mL of the acid had evaporated the contents were cooled, diluted with water and transferred over a filter paper. The carbon sample was washed exhaustively with hot distilled water until the filtrate was free of nitrate ions. This oxidation and washing resulted in the loss of some carbon. Some of the oxidized carbon also passed through the filter paper. The washed carbon sample was dried first in air and then in an electric oven at 120°C, outgassed at 150°C and then stored in stoppered glass bottles flushed with nitrogen.

### Oxidation with oxygen gas

5 g of each carbon sample was spread in a platinum boat. The mouth of the platinum boat was covered with a platinum lid having holes so that oxygen gas could make contact with the carbon. The boat containing the carbon sample was placed in a resistance tube furnace. The temperature of the furnace was maintained at 350 C. Pure and dry oxygen was passed over the sample at the rate of 2 Lh<sup>-1</sup> for 4 hrs. The sample was then cooled in oxygen gas and transferred to reagent bottles and stored under nitrogen.

### Degassing of the carbon

About 5 g of each of the activated carbon sample was spread in thin layer about 5 inches long in a tube furnace. It was kept in position by means of porous copper gauge plugs. The tube furnace was connected to a Hyvac. Cenco vacuum pump capable of giving a vacuum to the order of  $3 \times 10^{-3}$  mm Hg. The temperature of the furnace was raised to the required level slowly. The gases begun to be evolved soon after. The temperature was allowed to rise gradually and before it was raised by another  $50^\circ\text{C}$  complete elimination of the gases, at the proceeding temperature was ensured. After degassing at the required temperature, the sample was allowed to cool in vacuum to room temperature to avoid reformation of the carbon-oxygen surface groups and was then transferred to stoppered bottles flushed with nitrogen. These samples are referred to as 'degassed samples' in the text.

#### Determination of pH of the carbon Adsorption of Cobalt (II) ions

The adsorption of Co(II) ions was determined by placing a known weight (0.5g) of each carbon sample, (dried in an electric oven at  $120^\circ\text{C}$  and cooled in a desiccator) with 50 ml solutions of cobalt nitrate of different concentrations. The suspensions were placed in an air thermostat maintained at  $30 \pm 1^\circ\text{C}$ . The suspensions were shaken occasionally. After 24 hrs. an aliquot portion of the supernatant liquid was pipetted out and the concentration determined spectrophotometrically using a Hitachi 330 double beam spectrophotometer at a wavelength of 425 nm using standard analytical procedures (Vogel, 1989).

## RESULT AND DISCUSSION

### Adsorption Isotherms

The adsorption isotherms of Co(II) ions from aqueous solutions of cobalt nitrate in the concentration range 20-1000 mg/L on two samples of granulated activated carbons (GAC-E and GAC-S) and two samples of activated carbon fibers (ACF- 307) and ACF- 310) are presented in Fig. 1. The pH of each solution was maintained at 5 by the addition of nitric acid. It is seen that the adsorption isotherms are Type - I of the BET classification showing an initial rapid adsorption tending to be asymptotic at higher concentrations. the adsorption may be described by the general Langmuir equation.

$$\frac{X}{X_m} = \frac{bC^n}{1+bC^n}$$

Where x is the amount adsorbed at equilibrium concentration C,  $X_m$  is the maximum amount of Co(II) adsorbed, b is the Langmuir constant and n is the parameter which characterizes the quasi-Gaussian energetic heterogeneity of the adsorbent surface. When  $n=1$  the above equation is reduced to the classical Langmuir isotherm equation characteristic of homogenous surfaces. But only few surface are energetically homogenous and therefore, n is usually less than unity.

At lower concentration the term  $bC^n$  is very small and the Langmuir equation reduces to the Freundlich equation.

$$\frac{X}{X_m} = bC^n$$

Which is frequently used for the interpretation of adsorption from solutions because of its simplicity. The Freundlich isotherm equation is generally written as:

$$X = kC^n \text{ (where } X_m b = k \text{)}$$

k in the equation is the Freundlich isotherm equation constant and is related to the adsorption energy. The logarithmic form of the Freundlich equation can be expressed as:

$$\log x = \log k + n \log C$$

The linear Freundlich isotherms on log - log scale for the adsorption of Co(II) ions on the four as-received activated carbon samples are shown in Fig. 2. The parameters  $X_m$  and n as calculated from the linear Freundlich plot are recorded in Table 1. It is seen that the value of n which is a measure of surface heterogeneity is always less than unity which indicates that none of the activated carbons has a completely homogenous surface. This can be attributed to the fact all the activated carbons are associated with certain amounts of oxygen present at certain sites on the carbon surface in the form of carbon-oxygen surface groups which render the carbon surface heterogeneous in character. Similar linear Freundlich adsorption isotherms were plotted for carbon samples after oxidation of the activated carbons and after degassing of the oxidized carbon samples. It was observed that while the value of n decreased on oxidation due to the elimination of additional carbon oxygen surface groups, the value of n increased on degassing due to the elimination of these surface groups. The value of n was at a minimum for the carbon samples oxidized with nitric acid which incidentally results in the fixation of maximum amount of oxygen on the carbon surface. The value of n was the highest and close to unity for the  $950^\circ$ -degassed carbon samples which had lost the chemisorbed oxygen almost completely. This indicated that the  $950^\circ$ -degassed samples had more or less a homogenous surface.

### Influence of Surface area on the Adsorption

It is also seen from the adsorption isotherms in Fig. 1 that all the activated carbons, granulated as well as fibrous, adsorb appreciable amounts of Co(II) ions and that the amount adsorbed at each concentration is different for different carbons. In general, the granulated activated carbons adsorb larger amounts of Co(II) ions compared to activated carbon fibres. The adsorption on GAC-S is more than three times the adsorption on ACF-307 although the surface area of ACF-307 ( $910 \text{ m}^2/\text{g}$ ) is only  $\sim 25\%$  less than that of GAC-S ( $1256 \text{ m}^2/\text{g}$ ). Similarly ACF-310 and GAC-E, although have similar surface areas ( $1184$  and  $1190 \text{ m}^2/\text{g}$ ) show widely different adsorptions. This indicates that the adsorption of Co(II) by the activated carbons can not be explained on the

basis of surface area alone. This is further supported by the uptake of Co(II) on the oxidized carbon samples. The adsorption of Co(II) increases an oxidation although, the surface area of the oxidized samples are lower than those of the as received carbon samples. This aspect has been discussed a little later in the text. It appears that the adsorption of Co(II) surface area alone. This is further supported by the uptake of Co(II) on the oxidized carbon samples. The adsorption of Co(II) increases an oxidation although, the surface area of the oxidized samples are lower than those of the as received carbon samples. This aspect has been discussed a little later in the text. It appears that the adsorption of Co(II) is also influenced by the chemical nature of the carbon surface. As these activated carbons have been prepared using different raw materials and using different preparation procedures, the chemical structure of their surface is likely to be different.

### Influence of Carbon-Oxygen Surface Groups

It is well known that activated carbons are invariably associated with certain amounts of chemisorbed oxygen, the amount depending upon the source raw material and the history of their preparation (Bansal *et al.* 1978, 1988, 2001). This oxygen is present in the form of carbon-oxygen functional groups, some of which are acidic in character. The acidic surface groups are evolved as  $CO_2$  on evacuation in the temperature range 400-750°C and have been postulated as carboxyls and lactones (Bansal *et al.* 1978, 1988 Garten and Weiss 1957, Boehm *et al.* 1966, Barton *et al.* 1978,). The other oxygen surface groups are evolved as CO on evacuation in the temperature range 500-950°C. These groups have been postulated to be quinones and tend to make the carbon surface hydrophobic and neutral in character. Furthermore, the amounts of these surface oxygen groups can be enhanced on oxidation depending on the nature and strength of the oxidative treatment and reduced on degassing the oxidized carbons.

The amounts of these acidic and non-acidic surface groups which are evolved as  $CO_2$  and CO on degassing were determined and are given in Table 2 for the as-received carbons, it appears (that the presence of acidic surface groups has a larger influence on the adsorption of Co(II) from aqueous solutions.

In order to investigate the influence of carbon-oxygen surface functional groups on the adsorption of Co(II) more clearly, two of the activated carbons were oxidized with nitric acid in the liquid phase and with gaseous oxygen at 350°C. The adsorption isotherms on the oxidized samples are shown in Fig 3 for ACF-307 and in Fig. 4 for GAC-E. The adsorption isotherms on the as-received samples are reproduced in these figures for the sake of easy comparison. It is evident that for both the activated carbons, the adsorption increases considerably on oxidation, the magnitude of increase being different for the two oxidative treatments. The adsorption increases from 0.9% to 1.2 and 2.9% in the case of ACF-307 and from 2.1% to 2.3 and 3.4% in the case of GAC-E respectively on oxidation with oxygen gas and nitric acid. It is interesting to note that the uptake of Co (II) is considerably larger when the oxidation is carried out with nitric acid. This may be attributed to the fact that the treatment

**Table 1**  
Parameters of Freundlich adsorption isotherms on four different as received activated carbons.

Sample	$X_m$ (mg/g)	n
GAC-S	38.5	0.41
GAC-E	21.2	0.39
ACF-307	22.3	0.38
ACF-310	9.4	0.37

**Table 2**  
Surface areas and gases evolved on degassing different as received activated carbons at 950°C.

Sample Identification	BET ( $N_2$ ) Surface area ( $m^2/g$ )	Oxygen evolved as (g/100g)			
		$CO_2$	CO	$H_2O$	Total
ACF-307	910	1.00	5.30	1.30	7.60
ACF-310	1184	1.90	4.20	1.40	7.50
GAC-S	1256	2.10	1.05	.124	4.39
GAC-E	1190	2.13	1.66	1.33	5.12

**Table 3**  
Gases evolved on degassing different as received and oxidized activated carbons at 950°C.

Sample Identification	BET Surface area ( $m^2/g$ )	$CO_2$	Oxygen evolved as (%)		
			CO	$H_2O$	Total
ACF-307					
As-received	910	1.00	5.30	1.30	7.60
$HNO_3$ -oxidised	840	12.90	7.47	2.40	22.77
$O_2$ -oxidised	860	3.11	7.71	1.20	12.02
GAC-E					
As-received	1190	2.13	1.66	1.33	5.12
$HNO_3$ -oxidised	1100	12.40	6.20	1.92	20.52
$O_2$ -Oxidised	1042	3.17	5.97	1.26	10.40

with nitric acid is a stronger oxidative treatment and results in the formation of considerably larger amounts of carbon-oxygen surface groups in both the carbons (Table 3). The amount of associated oxygen increases from 5-7% to between 20-23% on oxidation of the two carbons.

Furthermore, it is also evident from Table 3, that the oxidation with nitric acid enhances the amount of surface acidic groups by several times while the increase on oxidation with oxygen gas is only small. The non-acidic surface groups although increase on both the oxidations, their values are more or less of the same order for each oxidative treatment. Thus it appears that the increase in adsorption of Co(II) ions which is much larger in the case of carbon samples oxidized with nitric acid is due to the presence of larger amounts of the surface acidic functional groups.

This view is further supported by the adsorption isotherms on the oxidized

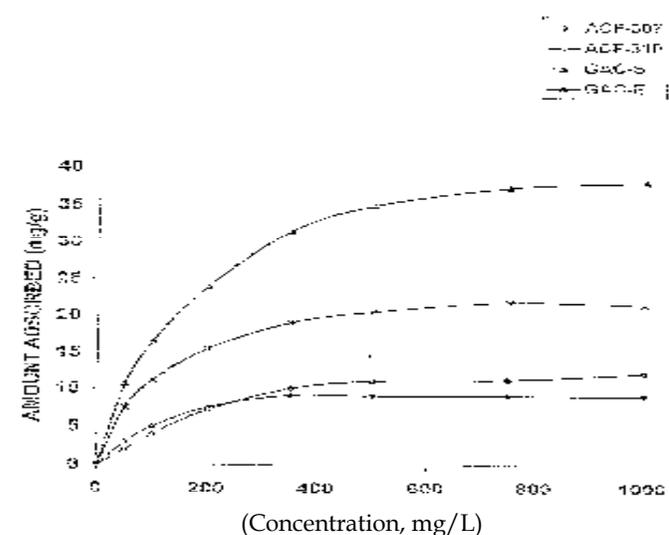
**Table 4**  
Gases evolved on degassing different oxidised and degassed  
ACF- 307 carbon samples at 950°C

Sample Identification	CO <sub>2</sub>	Oxygen evolved as (g/100 g)		
		CO	H <sub>2</sub> O	Total
ACF-307				
HNO <sub>3</sub> oxidised and then degassed at (°C)	12.90	7.47	2.40	22.77
400	10.85	7.35	0.85	19.05
650	2.15	6.86	0.12	9.13
950	-	Traces	-	-
Oxygen oxidised and then degassed at (0C)	3.11	7.71	1.20	12.02
400	2.95	8.15	0.82	11.92
650	0.42	7.81	0.21	8.44
950	-	Traces	-	-

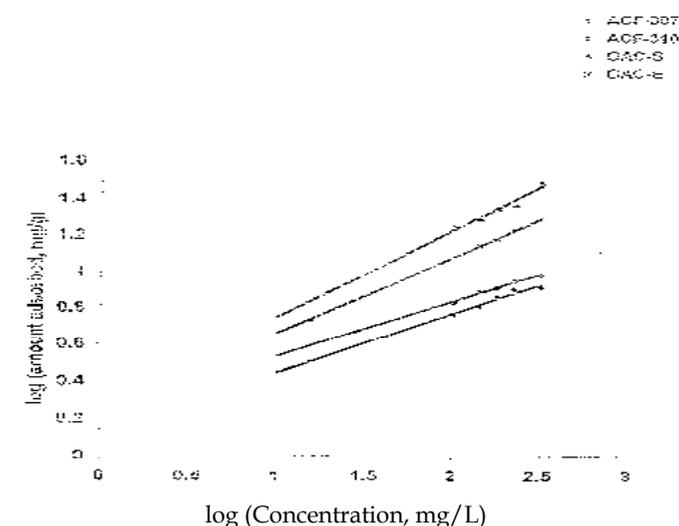
**Table 5.** Gases evolved on degassing different oxidised and degassed GAC-E carbon samples at 950°C.

Sample Identification	CO <sub>2</sub>	Oxygen evolved as (g/100 g)		
		CO	H <sub>2</sub> O	Total
GAC-E				
HNO <sub>3</sub> oxidised and then degassed at (°C)	12.40	6.20	1.92	20.52
400	10.85	5.92	1.02	17.79
650	2.15	6.86	0.12	9.13
950	Traces	Traces	Traces	Traces
Oxygen oxidised and then degassed at (0C)	3.11	7.71	1.20	12.02
400	2.86	5.56	1.00	9.42
650	0.58	4.78	0.62	5.98
950	-	Traces	-	-

carbon samples degassed at gradually increasing temperatures of 400°, 650° and 950°C (Figs. 5 to 8 ). This treatment eliminates varying amounts of the different carbon-oxygen surface groups depending upon the temperature of degassing. It is seen that the adsorption of Co(II) decreases gradually as the temperature of out gassing is enhanced. The decrease in adsorption is very small both for ACF-307 and GAC-E when degassing is carried out at 400°C. This is due to the fact that degassing at 400°C eliminates only a small part (~ 15%) of the acidic carbon-oxygen surface groups (Table 4 and 5) However, when the oxidized samples are degassed at 650°C, a temperature at which a major portion (~ 85%) of the acidic surface groups are removed as CO<sub>2</sub>, the adsorption of CO(II) decreases considerably although these samples still retain a larger portion of the non-acidic surface groups evolved as CO. In the case of 950° - degassed samples the adsorption of Co (II) ions is even smaller. This can be attributed to the fact that these samples are almost completely



**Fig. 1** Adsorption Isotherms of CO(II) ions on different as received activated carbons.



**Fig. 2** Freundlich adsorption isotherms of CO(II) ions on different activated carbons.

free of the associated oxygen which provides sites for the adsorption of Co (II) ions. The adsorption of Co(II) in the case of the 950° - degassed samples is even smaller than that on the as - received samples because the latter samples do contain small amounts of acidic carbon-oxygen surface groups. Whatever adsorption takes place in the 950° degassed carbon samples may be attributed to adsorption in the micropores of these carbons. Thus it is apparent that the adsorption of Co(II) ions is determined largely by the presences of oxygen surface groups and more so by the presence of those oxygen groups which are acidic in character and are evolved as CO<sub>2</sub> on degassing.

Whatever adsorption takes place in the 950° degassed carbon samples

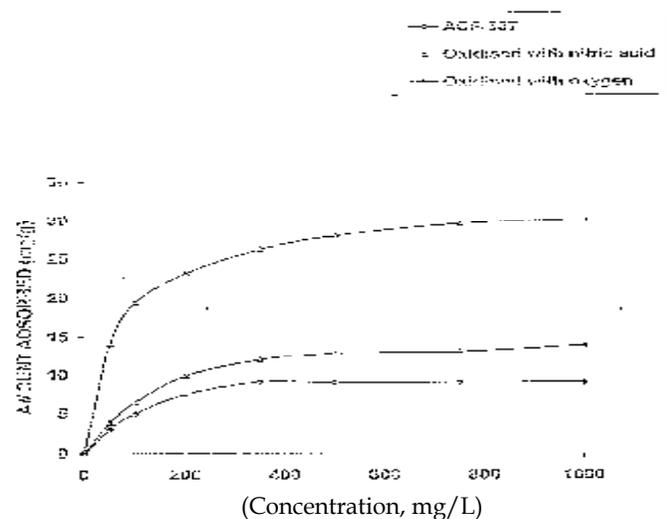


Fig. 3 Adsorption isotherms of CO(II) ions on ACD-307 before and after oxidation.

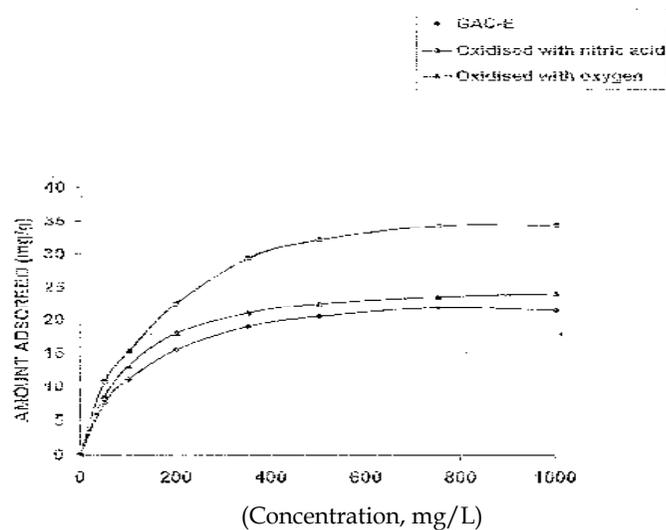


Fig. 4

may lie attributed to adsorption in the microprocs of these carbons. Thus it is apparent that the adsorption of Co(II) ions is determined largely by the presences of oxygen surface groups and more so by the presence of those oxygen groups which are acidic in character and are evolved as  $\text{CO}_2$  on degassing.

#### Influence of Solution pH on the Adsorption

The presence of acidic carbon-oxygen groups on the surface of activated carbons and their ionization in water also changes the pH of the carbon suspension. The pH of the as-received ACF-307 suspension in water was about 7 while that of GAC-1: was about 10. However, the pH of these carbon

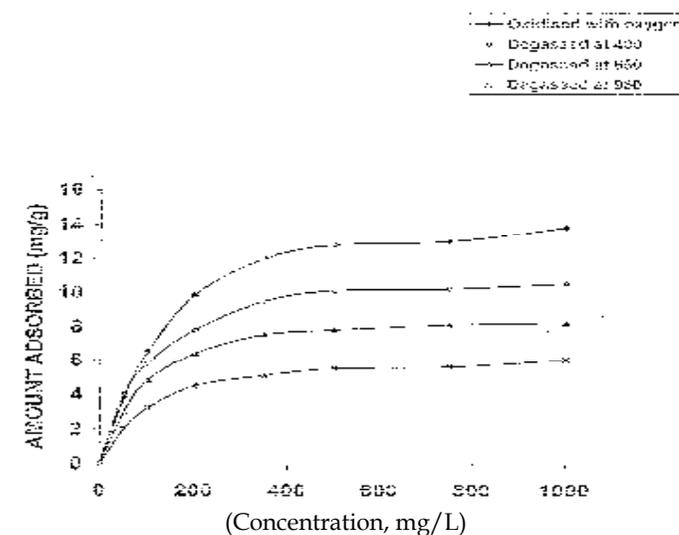


Fig. 5 Adsorption isotherms of Co(II) ions on aCD-307 oxidised with oxygen gas before and after degassing

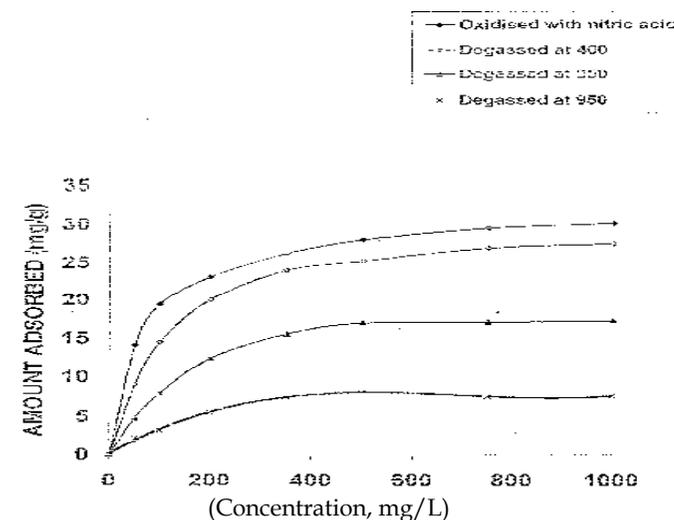


Fig. 6 Adsorption isotherms of Co(II) ions on ACF-307 oxidised with nitric acid before and after degassing.

suspensions decreased to between 3 and 4 on oxidation with nitric acid and to between 4 and 5 on oxidation with oxygen gas. Thus the increase in adsorption of Co(II) ions on oxidation of the carbons is due to the interaction of Co(II) ions with the carbon-oxygen surface groups as well as due to the modification of the solution pH. The effect of solution pH on the uptake of Co(II) is shown in Fig 9. It is seen that the uptake of Co(II) increases as the pH is increased up to a pH of about 6 and decreases at higher pH values. This shows that a change in pH of the solution results in a change in the carbon surface charge, which is different at different solution pH values (Goyal *et al.*

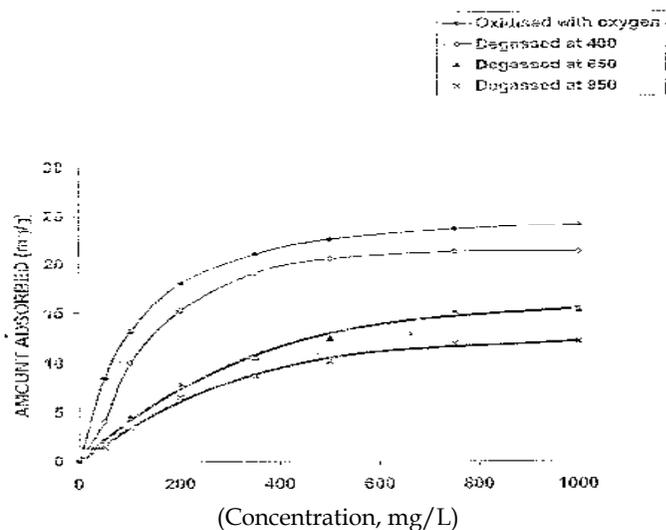


Fig. 7 Adsorption isotherms of Co(II) ions on GAC-E oxidised with oxygen gas before and after degassing.

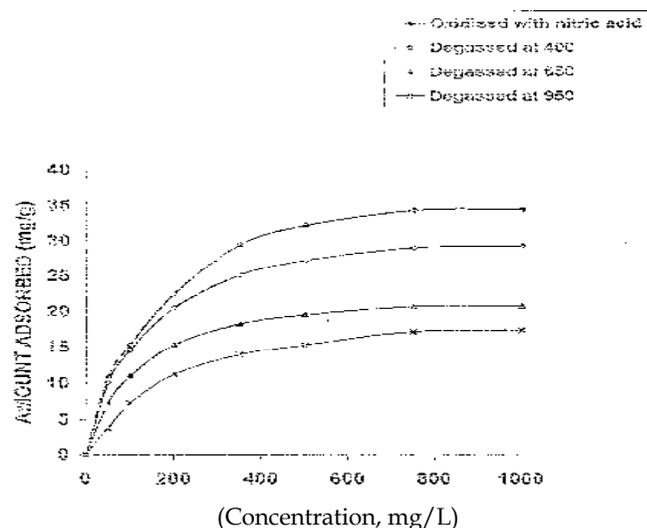


Fig. 8 Adsorption isotherms of Co(II) ions on GAC-E oxidised with nitric acid before and after degassing.

1999, 2001, Radovic et al 2001, Aggarwal et al. 1999, Aggarwal et al. 1999). A sudden increase in the adsorption of Co(II) ions in the pH range 3-4 indicates that the zero point charge (ZPC) of the carbon surface lies between these pH values. At pH values lower than ZPC, there is excessive protonation of the carbon surface which gives it a positive charge. This enhances the electrostatic repulsive interactions between the carbon surface and the positively charged Co(II) cations and results in lower adsorption. As the which have been postulated as carboxyls and lactones. These surface oxygen groups on ionization

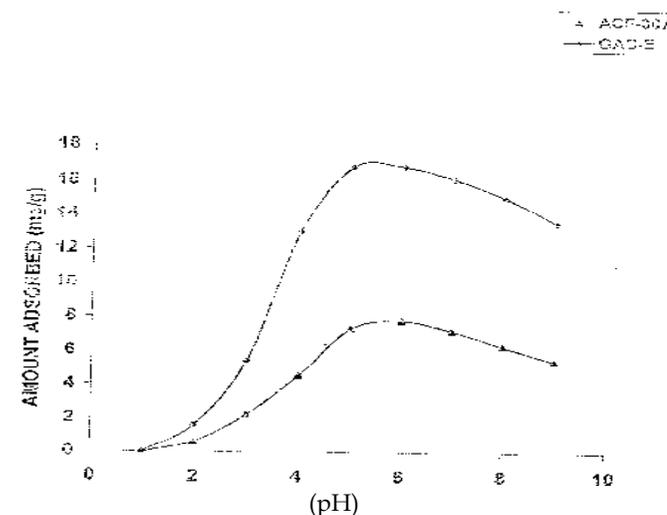


Fig. 9 Effect of solution pH on the adsorption of Co(II) ions.

in aqueous solutions produce  $H^+$  ions which are directed towards the liquid phase leaving the carbon surface with negatively charged  $-COO^-$  sites. The carbon surface of oxidized carbons, therefore, behaves as negatively charged. This increases the electrostatic attractive interactions between the negatively charged carbon surface and the positively charged Co(II) cations thereby increasing the adsorption of Co(II) ions. On degassing of the activated carbons at gradually increasing temperatures, these acidic surface oxygen groups are eliminated gradually and this results in a decrease in the number of the negatively charged sites which in turn decreases the uptake of Co(II). When the surface oxygen groups are removed almost completely by degassing at  $950^\circ C$ , the concentration of negatively charged  $COO^-$  sites is reduced to almost nil and the carbon surface attains more or less a positive character. This decreases the attractive interactions between the carbon surface and the Co(II) ions thereby decreasing the adsorption further. The adsorption of Co(II) ions in the case of  $950^\circ C$ -degassed carbons may be attributed to take place in pores.

Thus the results presented in this paper show clearly that the adsorption of Co(II) from aqueous solutions by activated carbons is determined mainly by the acidic carbon-oxygen surface groups.

#### ACKNOWLEDGEMENT

The authors are thankful to Norit N.V. Netherlands and the Ashland Company USA for the gift of activated carbons. The authors are also thankful to Defence Research and Development Organization for the award of Research Project No. ERIP/ER/0103320/M/01

#### REFERENCES

Aggarwal, D., Goyal, M. and Bansal, R.C. 1999. *Carbon*. 37 : 1989.

- Bansal, R.C. Bhatia, N. and Dhama, T.L. 1978. *Carbon*. 16 : 65.
- Bansal, R.C. Dhama, T.L. and Parkash, S. 1978. *Carbon*. 16 : 289.
- Bansal, R.C., Donnet, J.B. and Stoeckli, F. 1988. *Activated Carbon*. Marcel Dekker, Inc. New York
- Barton, S.S., Gellispic, D.H., Harrison, B.H. and Kcmp, W. 1978. *Carbon*, 16: 363.
- Boehrn, H.P. 1966. *Advances in Catalysis* Vol. 16 Acad Press, New York 179.
- Garten, V.A. and Weiss, D.E. 1957. *Rev. Pure Appl. Chem.* 7 : 69.
- Goyal, M., Rattan, V.K. and Bansal, R.C. 1999. *Indian J. Chem. Technol.*, 6: 305.
- Goyal, M., Rattan, V.K., Aggarwal, D. and Bansal R.C. 2001. *Colloid and Surfaces A Physico-Chemical and Engg. Aspects*. 190 : 229.
- Kaya, M. and Akyol, F. 1992. *Kim Kim Muhendisligi Semp.* 8<sup>th</sup> 3 : 213.
- Kim, U.S., Ryu, S.K., Park, K.K., Lee, J.B. and Jung, C.H. 2002. *Carbon*. 02, Intern. Conf. On Carbon, Beijung. 191 : 0098.
- Netzer, A. and Hughes, D.E. 1984. *Water Res.* 18 : 927.
- Paajanon, A., Lehte, J., Sautpakka, T. and Morneau, J.P. 1997. *Sep. Science Tehcnol.*, 32 : 2077.
- Puri, B.R., and Bansal, R.C. 1964. *Carbon*, 1: 451.
- Puri, B.R. 1970. in "*Chemistry and Physics of Carbon*" (P.L. Walker Jr. Edit) Marcel Dekker, Inc. New York 6: 191.
- Radovic, L.R., Morino-Castilla, C. and Rivera-Utrilla, J. *Chemistry and Physics of Carbon*. (L.R, Radovic Edit) Marcel Dekker, New York 27 : 227.
- Rivera-Utrilla, J. and Ferro-Garcia, M.A. 1987. *Carbon*. 25 : 645.
- Shakir, K., Benyamin, K. and Aziz, M. 1993. *J. Radioanal. Nucl. Chem.*, 173 : 141.
- Shakir, KL, Flex, H. and Benyamin, K. 1993. *J. Radioanal. Nucl. Chem.* 173 : 303.
- Takiyama, LR. and Huang, CP. 1997. 23<sup>rd</sup> Bienn. Conf. Carbon. The Penn. Stale Univ. University Park, Pennsylvania July 13-17,
- Tekker, M., Sallakar, O. and Imamoglu, M. 1977. *J. Environ Sciecn Health A*, 32 : 2077.
- Vogel, I. 1989. *Text Book of Quantitative Chemical Analysis*. (Revised by G.H. JaQTcry, J. basset, J. Mendham and R.C. Denncy) ELBS, Longman, England 5<sup>th</sup> Edition 668.