

ADSORPTION OF CHROMIUM IONS FROM AQUEOUS PHASE ONTO ACTIVATED CARBONS: EFFECT OF SURFACE OXYGEN COMPLEXES.

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Introduction

Chromium is one of the major trace metals present in water effluents from different industries like leather, textile, chemical manufacture, metal finishing and many other industries. Activated carbon is widely used to remove inorganic pollutants from water, due to the fact that these materials are unique and versatile adsorbents because of their high adsorption capacity, and surface chemical nature [1]. In the case of the adsorption of inorganic compounds on activated carbons from aqueous solutions, the surface chemical nature of the adsorbent i.e., surface oxygen complexes [1,2], has in general, more influence than the surface area and porosity of the adsorbents. Therefore, the objective of the present study is to assess how the surface nature i.e. surface oxygen complexes of activated carbons affect the adsorption process.

Experimental

The investigations reported in this paper were conducted on two different types of activated carbon samples. One is fiberbased activated carbon, which referred as OA (activated charcoal cloth), and the other one is granular activated carbon referred as OG. In order to introduce surface oxygen complexes these carbon samples were oxidized with different oxidizing agents like HNO_3 , H_2O_2 and $\text{NH}_4(\text{S}_2\text{O}_4)_2$. The detail of these procedure has been reported elsewhere [2]. The activated samples oxidized with nitric acid referred as AN and GN and these oxidized samples heat treated at 600 °C under nitrogen flow were referred as AN600 and GN 600 respectively. When activated carbon samples were oxidized with H_2O_2 and $\text{NH}_4(\text{S}_2\text{O}_4)_2$ referred as AH, GH and AS, GS respectively. Elemental analysis of C, H, N, O (by difference) of the activated carbon samples was carried out on the Perkin Elmer 240 °C Elemental Analyzer. The surface acidity was determined by using Boehm method. The activated carbon samples were characterized by N_2 adsorption gravimetrically at 77 K after preheating at 150 °C and 10 mPa for 10 h by using a CAHN 2000 vacuum electromicrobalance system. The specific surface area and micropore volume was obtained by using BET and DR methods. The adsorption processes from aqueous solutions of the chromium ions on the activated carbons were carried out at 300 K by batch method. For this purpose, aqueous solutions with different initial concentrations of $\text{Cr}(\text{NO}_2)_3 \cdot 9\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{CrO}_4$ were used. Adsorption isotherms were determined by using stoppered flasks containing 0.1g of activated carbon/50 ml of

solution. They were kept in a thermostat shaker bath at 300 K for 24 hours, after which the equilibrium concentration was determined by atomic absorption spectrometry by using an EC-ASS-4129 model atomic absorption spectrometer. All isotherms were determined without adding any buffer to control the pH in order not to introduce a new electrolyte in the system.

Results

Characterization of activated carbons. The acidic surface oxides measured by Boehm's method and the elemental analysis of all activated carbon samples were shown in Table 1. From the Table 1, it is observed that there is an increase in the amount of oxygen in the oxidized sample, which is maximum in the case of the sample oxidized with HNO_3 and minimum in the case of H_2O_2 . When the oxidized samples were heat treated at 600 °C, their oxygen percentage was found to decrease. The selective base neutralization method gives information on oxygen surface functionality of the activated carbon studied. The original carbon samples show some acidity which can originate from precursor characteristics, but also the degradation condition and the storage conditions of the activated carbon sample. The acidity enhancement is evidently due to the oxidation of the samples. The total acidity of the carbon oxidized by HNO_3 is maximum and three times that of the original in both cases. In these samples stronger acidic groups were predominated. Same tendency also observed with the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ oxidized samples. But the H_2O_2 oxidized samples have almost same or a little bit more acidity than the original carbons. In all the case the amount of weak surface oxygen groups is smaller. When the oxidized samples were heated under N_2 at 600 °C, the total acidity decreased drastically, which indicates the removal of some carbon-oxygen surface group.

Adsorption isotherm of Cr ions. The adsorption isotherms of Cr(III), from aqueous solution onto different activated carbon samples having different surface oxygen complexes are shown in the Figure 1. The isotherms obtained were of the L type from Giles et al. classification. They were very well fitted with Langmuir isotherm. The adsorption capacity of the original activated carbon samples is lower than those of oxidized samples, in spite of the fact that the surface area and porosity of oxidized samples are lower than those of the original sample are. This cannot be explained on the basis of surface area and porosity alone, hence can be

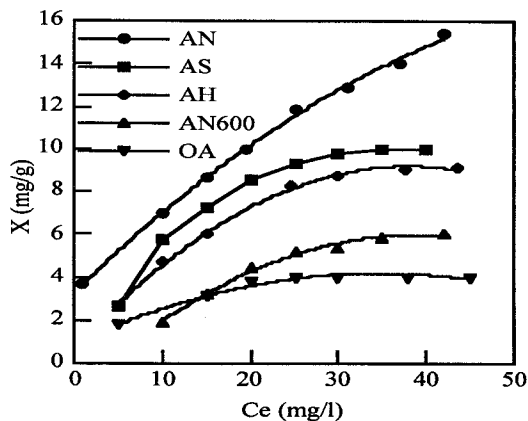


Figure 1. Adsorption isotherms for Cr(III) from aqueous solution at 300 K.

attributed to the presence of the surface oxygen groups of acidic character created during the oxidation of original samples with different oxidizing agents like HNO_3 , H_2O_2 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ which play a role in determining the adsorption of these carbon for Cr(III) ions. It is seen from the base neutralization, that the activated carbon samples oxidized with nitric acid have maximum surface acidity. The adsorption capacity of the activated carbon samples are in the following order: AN > AS > AH > AN600 > OA. The acidic groups present on the surface of activated carbons would be dissociated in aqueous solution forming their conjugate bases and becomes the specific sites to adsorb Cr(III) ions. The oxidation of the activated carbon changed the nature of the activated carbon to hydrophilic from hydrophobic, decreasing the pH of the activated carbon suspension. These changes favor the adsorption process. When the oxidized samples (nitric acid) is heat-treated to a temperature 600 °C, most of the carboxylic groups were eliminated. The adsorption capacity of these activated carbon samples for Cr(III), was drastically reduced in spite of an increase in the surface area and the porosity of this samples as compared to

those of oxidized activated carbon samples. These data clearly show the importance of the surface chemical nature of the activated carbon on the adsorption process of Cr(III). The adsorption isotherms of Cr(VI) on the activated carbons are of type L of the Giles classification and are very well fitted by the Langmuir equation. The adsorption capacity of the original activated carbon samples is lower than those of oxidized one, in spite of the fact that the surface area and porosity of oxidized samples are lower than those of the original sample are. At first, this result seems to be contradictory, because the oxidized activated carbon samples have less affinity to specifically adsorbed anions than original sample due to its surface chemical nature. However, these results can be easily explained if Cr(VI), in presence of oxidized activated carbon samples, is partly reduced to Cr(III). This reduction takes place at acid sites on the surface of the carbon and perhaps by the -OH surface group of the activated carbon. This character of -OH groups has been described in the literature [1]. The adsorption capacity values show that the adsorption process of Cr(VI) followed the same order as that found for the adsorption of Cr(III).

Conclusions

These results clearly indicate that the removal of chromium either as Cr(III) or as Cr(VI), from aqueous solutions by activated carbons is greatly enhanced by the presence of surface oxygen complexes of acid type and is practically independent of their surface area and porosity of the activated carbon.

References

1. Bansal RC, Donnet JB, Stoeckli F. In: Active Carbon, Marcel Dekker, New York, 1988.
2. Pradhan BK, Sandle, NK, Effect of different oxidizing agents treatment on the surface properties of activated carbons, CARBON(in press).

Table 1. Elemental analysis, amount of surface acidic groups present analyzed by selective base neutralization, specific surface area and micropore volume of activated carbon samples.

Sample	weight % of the element				amount of reagents reacted (meq./100g)			S (m ² /g)	W _o (ml/g)
	C	H	N	O (by diff.)	NaOH	Na ₂ CO ₃	NaHCO ₃		
OA	87.7	0.8	2.2	9.3	160	116	114	1047	0.511
AN	68.6	0.7	3.3	27.4	567	346	342	432	0.270
AN600	74.3	0.1	2.5	23.1	360	152	136	736	0.353
AH	74.1	1.2	0.0	24.7	164	128	122	951	0.453
AS	68.8	1.5	0.2	29.5	496	478	465	798	0.374