

ADSORPTION OF COPPER IONS FROM AQUEOUS SOLUTION BY ACTIVE CARBONS

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Introduction

Active carbons are frequently used for the adsorption of metal ions from aqueous solution. Typical applications are for the removal of pollutant species from domestic water supplies and industrial effluents. It is usually assumed that the mechanism of adsorption is by polar or ionic interaction between the positively charged metal species and anionic oxide groups present on the carbon surface. Consequently, in order to improve metal ion uptake, carbons are frequently treated oxidatively e.g. using warm nitric acid, in order to increase surface polarity. Carbons so treated frequently display increased affinity for metal ions however, the type of surface functional groups present after oxidation are usually not known.

As a first step in understanding the individual interactions which govern metal ion adsorption by active carbon granules (ACGs) we have recently been studying the adsorptive properties of commercial, wood based, phosphoric acid activated ACGs. These materials have not been subjected to additional oxidation but do have varying levels of native chemisorbed oxygen. Aqueous copper II ions (CuNO_3 and CuSO_4) have been used as probes.

Experimental

A series of three wood based, phosphoric acid activated commercial carbons (*Westvaco Ltd.*) have been investigated. Porosity has been characterised from nitrogen adsorption data measured at 77 K. Surface chemistry has been studied using X-ray photoelectron spectroscopy (XPS) and the associated polarity of the carbons has been assessed by water adsorption at 293 K. Cu II adsorption isotherms in the concentration range 0 to 70 m.mol/l have been measured using a batch method whereby 0.1g of carbon was shaken for 16 hours with 10

cm³ of copper nitrate solution. Cu adsorption was calculated from the residual Cu II concentration of the supernatant measured by atomic adsorption spectroscopy. In addition, Cu II uptake has also been assessed by equilibrating 1g of each carbon in 100 cm³ of 10 m.mol/l CuSO_4 and measuring the Cu uptake as described above.

Results and Discussion

Structural data are given in Table 1. All 3 materials have similar micropore volumes although it can be seen that C48 contains about 25% more mesoporosity than the other 2 carbons.

Table 1. Structural Characteristics from N₂ adsorption

Carbon	C47	C48	C49
Micropore volume (<2nm) cc/g	0.21	0.20	0.22
Mesopore volume (2050nm) cc/g	1.03	1.26	1.01
Surface area M ² /g (BET)	1611	2079	1704
Mean particle diameter/mm	1.17	0.51	1.61

Table 2 shows the surface compositions of both granular and ground carbons determined by XPS.

Table 2. Elemental Compositions (atomic%) by XPS

	%C	%O	%P
C47	94.2	5.8	-
C48	98.2	1.8	-
C49	87.4	8.6(11.8)	0.8
C47 ground	95.8	4.2	-
C48 ground	97.5	2.5	-
C49 ground	88.6	6.9(10.5)	0.9

C48 contains least chemisorbed oxygen and C49 the most. C49 also shows some residual phosphorous which the P2p XPS peak indicates this to be present as phosphate which is presumed to be residual from activation. Assuming P as PO₄ the contribution to the total oxygen level is 3.2 at.% and therefore the carbon-oxygen level 8.6 at.%. A similar adjustment has been made for the ground sample of this material. In both instances the PO₄ may affect the polarity of the carbon. These overall compositional trends are also observed for the ground samples.

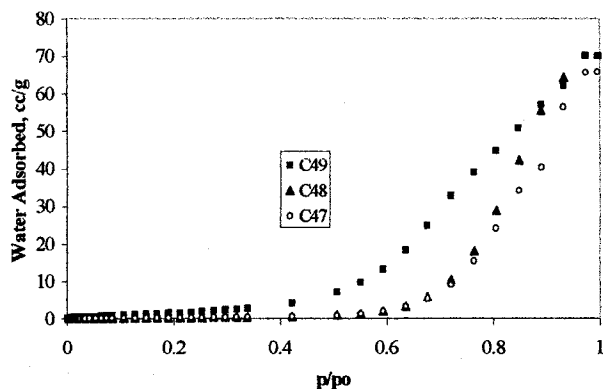


Figure 1: Water adsorption Isotherms at 293K

The water adsorption isotherms (Figure 1) reflect the higher oxygen level of the C49 carbon (seen clearly in Figure 2 which shows the $p/p_o < 0.35$ region of the isotherms). However, the adsorption isotherms for C47 and C48 are very similar with C47 appearing as the least polar. The desorption data (not given) show substantial hysteresis for C48 which is consistent with its greater mesoporosity.

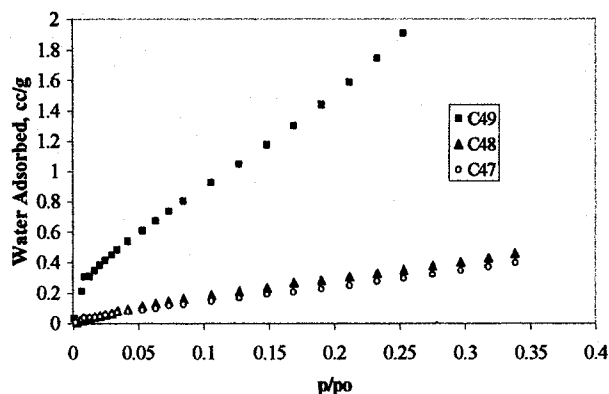


Figure 2: Water adsorption Isotherms at low p/p_o

On these data alone, and given the trends described in some existing literature, it would be tempting to predict that C49, with the greater polarity, would adsorb the most Cu II. Figure 3 shows that this is not the case and that in

fact C49 is the worst Cu adsorber of this sample set. C48 with the least apparent chemisorbed oxygen and relatively low polarity adsorbs more Cu ions over the concentration ranges studied than the other 2 materials. This rank has been confirmed using a second series of batch experiments whereby CuII was adsorbed from 10 m.mol/l CuSO₄ (see Figure 4).

The data presented therefore show no correlation between Cu II adsorption and total native surface oxygen levels or polarity of the carbons. Significantly, in these experiments the best adsorbent for Cu II contains the least chemisorbed oxygen. This behaviour may however be explained by the chemical states of the oxygen present on the respective carbons. Analysis of carbon 1s XPS data reveals that for C49 a significant portion of the oxygen present is in the form of COR and C=O groups whilst for C48 the carbon surface appears to be more acidic. It seems most probable that the Cu II ion interacts with acidic sites of the carbon structure possibly to form COO-Cu⁺ type structures. Since vigorous oxidation of carbons e.g. by nitric acid treatment, is known to produce predominantly COOH groups the improved adsorptivity of metal ions by carbons so treated can be explained.

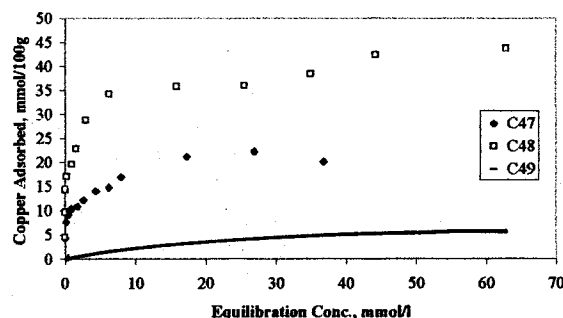


Figure 3: Copper Adsorption Isotherms

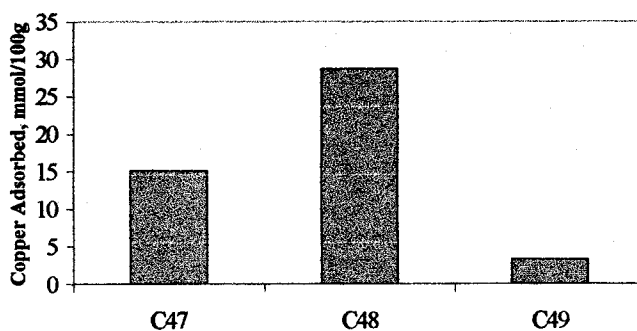


Figure 4: Comparison of Cu(II) uptake from 10 mmol/l CuSO₄