

THE EFFECT OF NITROGEN FUNCTIONALITY IN ACTIVATED CARBON ON THE ADSORPTION OF TRANSITION METAL CATIONS

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Introduction

The adsorption of inorganic or ionic species on activated carbon from solution is usually dominated by the surface functional groups [1]. The most important applications of activated carbon to the adsorption of metal species from solutions are for the recovery of noble metals, treatment of waste water and preparation of metal catalysts supported on carbon. In this study, XANES was used to determine the nitrogen surface functional groups incorporated into the carbon by ammonia treatment and by using polyacrylonitrile (PAN) as precursor. The influences of nitrogen functionality on the adsorption of transition metal cations Cd^{2+} , Ni^{2+} and Cu^{2+} were investigated.

Experimental

Coconut shell carbon C was heated to 800 °C at a heating rate of 3 °C min^{-1} in flowing ammonia and held at maximum temperature for 3 hours. The sample was designated as CA. Carbon C was also treated by HNO_3 followed by ammonia treatment and the resultant sample was designated as CNA. PAN carbon was prepared by treating PAN at 250 °C in flowing air for 1 hour and activation at 900 °C using CO_2 for 5 hours. The resultant carbon was designated sample code PANC. The nitrogen X-ray absorption near edge structure (K edge) spectroscopy measurements were conducted using beam line Station 1.1 of the Synchrotron Radiation Source (SRS) at Daresbury Laboratory [2]. Boehm's titration method was used to determine the amounts of surface acidic and basic functional groups in carbon. The nitrate salts of cadmium, nickel and copper were used for the adsorption studies.

The mixture of carbon and solution was adjusted to pH 5 and was allowed to stand for 48 hours at 25 °C. ICP-AES was used to determine the amounts of metals adsorbed on carbon.

Results and Discussion

The elemental analysis and porous structure characterization data of the carbons used are shown in Table 1. It is evident that treatment with ammonia at 800 °C introduced appreciable amount of nitrogen into the carbon. More nitrogen was incorporated into the carbon when carbon C underwent an oxidation pre-treatment using HNO_3 prior to ammonia treatment. Both methods of ammonia treatment did not greatly modify the porous structures of the carbon. The surface areas decreased only slightly after treatment by ammonia. Activated carbon with well developed porosity and high nitrogen content was prepared from polyacrylonitrile using carbon dioxide as activating agent. The high amounts of nitrogen in carbons allowed the assessment of the role of nitrogen functional groups on the adsorption of metal cations.

Selective neutralization studies (see Table 1) show that all the activated carbons used in this study contain neither carboxylic acid nor lactone groups. Therefore the influence of nitrogen functional groups on the adsorption of metal cations can be assessed in the absence of surface acidic oxygen functional groups which may involve in ion exchange reaction with metal cations and may increase the adsorption capacity of metal cation species. All the carbons show basic properties which are ascribed to the presence of basic oxides, the π system of the graphene layers of the carbon and the surface nitrogen functional groups.

Table 1 Characterization data of the carbons used

Sample Code	Ultimate analysis (wt % daf)				Pore volume * ($\text{cm}^3 \text{g}^{-1}$)		D-R surface area ($\text{m}^2 \text{g}^{-1}$)	Acid and bases consumed			
	C	H	N	O	Micropore (CO_2 , 273 K)	Total pore (N_2 , 77 K)		HCl	NaHCO_3	Na_2CO_3	NaOH
				(by diff)				(meq g^{-1})			
C	96.1	0.4	0.3	3.2	0.321	0.323	683	0.40	0	0	0.50
CA	95.5	0.1	2.3	2.0	0.257	0.304	546	0.70	0	0	0.80
CNA	90.3	0.5	5.3	3.9	0.197	0.295	493	0.78	0	0	0.65
PANC	85.1	0.5	9.4	5.0	0.256	0.296	545	0.71	0	0	0.50

Figure 1 shows the nitrogen X-ray absorption near edge structure (XANES) spectroscopy results of the carbons. The three well resolved peaks at 399.8, 401.1 and 402.6 eV in the XANES spectrum of PANC are assigned to pyridinic and pyridone groups. The XANES spectrum of CNA shows two well resolved peaks at 399.7 and 401.8 eV and a weak peak at 404.4 eV. The former two peaks are assigned as pyridinic and pyridone functionality. The assignments of the nitrogen functionality are consistent with previous work [2].

The adsorption isotherms of cadmium, nickel and copper cations on C, CA, CNA and PANC are shown in Figure 2, 3 and 4 respectively. It is apparent that the adsorption capacities of the transition metal cations were enhanced by the surface nitrogen functionality incorporated through ammonia treatment (CA, CNA) or inherited from the precursor (PANC). The porous structure characteristics, *i.e.* surface area and pore volume were not found to correlate with the metal adsorption in contrast to Au/Ag adsorption [3]. The capacities of the adsorption of Cd^{2+} , Ni^{2+} and Cu^{2+} are in the following order: PANC > CNA, CA > C, consistent with the order of nitrogen contents of the carbons. The effects of incorporated nitrogen functionality on the adsorption of calcium cation were also investigated in this study. The results show that in contrast to the adsorption of transition metals, the ammonia treatment did not improve the adsorption of Ca^{2+} . Titration and TPD studies show that carbon CA, CNA and PANC

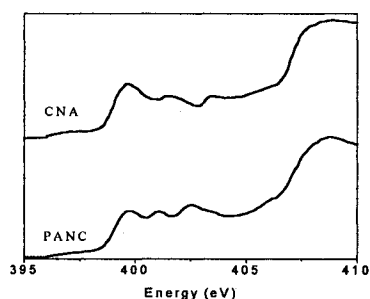


Figure 1 Nitrogen XANES spectra of CNA and PANC

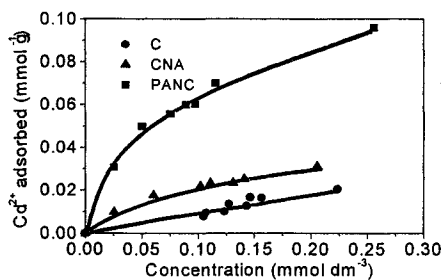


Figure 2 A comparison of Cd^{2+} adsorption on various carbons

are basic carbons. Therefore the enhancement of the adsorption capacities of heavy metals is mainly ascribed to the basic nitrogen functionality on the carbon surface. Nitrogen functional groups on the carbon surface can act as ligands which can coordinate with transition metal cations thereby increasing the adsorption capacities of Cd^{2+} , Ni^{2+} and Cu^{2+} .

Conclusions

Appreciable amounts of nitrogen functional groups can be incorporated into the carbon either by ammonia treatment or by using a nitrogen containing polymer precursor. They can act as ligands and enhance the adsorption of transition metal cations but not the alkali earth metals. However, carboxylic groups are more effective than nitrogen functional groups to enhance the adsorption of heavy metal cation species.

Reference

- [1] Bautista-Toledo I, Rivera-Utrilla J, Ferro-Garcia MA, Moreno-Castilla C. Carbon 1994; **32**:93-100.
- [2] Zhu Q, Money SL, Russell AE, Thomas KM. Langmuir 1997; **13**:2149-2157.
- [3] Jia YF, Steele, CJ, Hayward IP, Thomas KM. Carbon 1998; **36**:1299-1308.

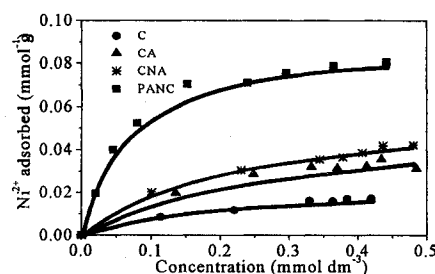


Figure 3 A comparison of Ni^{2+} adsorption on various carbons

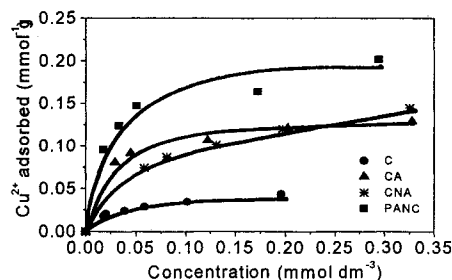


Figure 4 A comparison of Cu^{2+} adsorption on various carbons