

ADSORPTION OF CADMIUM CATIONS ON SURFACE OXYGEN SITES OF OXIDIZED ACTIVATED CARBON

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Introduction

The trace heavy metal cadmium present in waste water is of great concern from environmental prospective due to its toxicity. The use of activated carbon for the removal of the cadmium present in low concentration in aqueous solution is of considerable importance [1]. The objective of this work was to investigate the effects of oxygen functional groups incorporated into the active carbon by oxidation using aqueous nitric acid on the adsorption of cadmium cations.

Experimental

Coconut shell carbon C was treated using 7.5 M HNO₃ by refluxing for 48 hours. The oxidized carbon was Soxhlet extracted with water until a constant pH and was designated sample code CN. Carbon CN was heated at 10 °C under flowing helium to the desired temperature and held for 1 hour at the maximum temperature. The resultant carbons were designated as the code of original carbon followed by a number to indicate the heat treatment temperature in °C. Adsorption studies were carried out at 25 °C for 48 hours and desorption was carried out using Soxhlet extraction for 24 hours in water.

Results and Discussion

The analytical data, porous structure characteristics and titration results are shown in Table 1. It is apparent that treatment with nitric acid results in a large increase in oxygen and much smaller increases in nitrogen and hydrogen contents and decrease of carbon content. The oxidation treatment also decreased both the CO₂ micropore volume and N₂ total pore volume. Carbon C is a basic H-type carbon since it does not react with sodium carbonate and sodium bicarbonate. The oxidation by HNO₃ produced considerable amounts of acidic groups in the carbon with half of the total acidity in oxidized carbon being carboxylic groups as determined by the Boehm's method. Heat treatment led to progressive loss of acidic surface groups. The carboxylic acid groups are the most sensitive to heat treatment and approximately half of them in the oxidized carbon CN were removed by heat treatment at 300 °C, whereas the amounts of lactone and phenolic groups remained relatively unchanged at this temperature indicating they are more stable towards heat treatment.

The adsorption isotherms of cadmium on various carbons are shown in Figure 1. It is apparent that the adsorption capacity of cadmium was dramatically enhanced after carbon C was oxidized with HNO₃. After CN was subjected to progressive decomposition of surface oxygen functional groups by heat treatment at elevated temperature, the adsorption capacities of Cd²⁺ on the carbons were reduced significantly. The various types of oxygen surface groups do not make the same contribution

Table 1 The characterization data of active carbons used

Sample code	Amounts of acidic groups (meq g ⁻¹)			Ultimate analysis (wt %, daf)				Pore volume * (cm ³ g ⁻¹)		D-R Surface area (m ² g ⁻¹)
	Carboxylic acid groups	Lactone groups	Phenolic groups	C	H	N	O (by diff)	Micropore (CO ₂ , 273 K)	Total pore (N ₂ , 77 K) (CO ₂ , 273 K)	
C	0	0	0.50	96.1	0.4	0.3	3.2	0.321	0.323	683
CN	2.52	0.73	1.64	75.6	1.5	1.0	21.9	0.139	0.207	295
CN300	1.40	0.66	1.64	77.1	0.9	1.0	21.0	0.163	0.209	347
CN400	0.95	0.38	1.64	82.1	0.9	1.1	15.9	0.188	0.235	401
CN500	0.63	0.15	1.24	84.3	1.0	1.1	13.6	0.222	0.237	473
CN600	0.24	0.29	0.77	86.9	0.8	1.2	11.1	0.213	0.271	453
CN800	0	0	0.41	94.3	0.5	1.4	3.8	0.260	0.267	553

* Total pore volume was obtained from the amount adsorbed at p/p^o = 1 for nitrogen adsorption at 77 K, micropore volume was obtained from extrapolation of Dubinin-Radushkevich equation for carbon dioxide adsorption at 273 K

to the adsorption of cadmium. Carboxylic acid groups are the least thermally stable. Although heat treatment at 300 °C only decreased the oxygen content slightly, it produced the greatest reduction of cadmium adsorption capacity. This is indicative of oxygen present as carboxylic acid groups contributing most to the adsorption of cadmium.

The relation between the amounts of adsorbed cadmium and that of released protons after adsorption on CN is shown in Figure 2. It is evident that the ratio of released H^+ to adsorbed Cd^{2+} is approximately 2 in the lower concentration range used in this study. Little cadmium was desorbed from CN by Soxhlet extraction using water. Studies of CN after adsorption of cadmium followed by Soxhlet extraction with water show that cadmium is relatively uniformly distributed across the surface of the particle, indicating cadmium was adsorbed irreversibly on oxygen surface sites in the carbon. Therefore the carboxylic acid groups on the surface of CN are probably the main sites for the adsorption of cadmium cations with the ion exchange of Cd^{2+} with the H^+ of carboxylic acid group. Figure 3 shows the relation between the amounts of adsorbed cadmium on NaOH treated CN and that of released Na^+ . It is apparent that at lower concentration the amount of desorbed Na^+ is approximately twice that of

adsorbed Cd^{2+} , indicating that a cation exchange mechanism may be involved in the cadmium adsorption.

The possible modes of coordination of the carboxylate to the cadmium cation are illustrated in Figure 4, which represents the cation exchange reaction with one cadmium cation displacing two protons or sodium cations [2]. In the case of adsorption where H^+/Cd^{2+} or Na^+/Cd^{2+} ratios < 2 were observed, the nitrate anion may also be involved in order to balance the charge.

Conclusions

Oxygen functionality including carboxylic groups were incorporated into activated carbon by HNO_3 oxidation, which dramatically enhanced cadmium adsorption. The cadmium cation may be irreversibly adsorbed by ion exchange with protons of carboxylic groups.

Reference

- [1] Corapcioglu MO, Huang CP. Wat Res 1977;11:1031-1044.
- [2] Finnie KS, Bartlett JR, Woolfrey JL. Langmuir 1998; 14:2744-2749

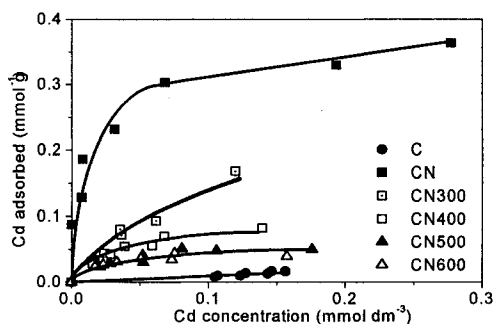


Figure 1 Comparison of adsorption isotherms of cadmium on carbon CN and heat treated derivatives

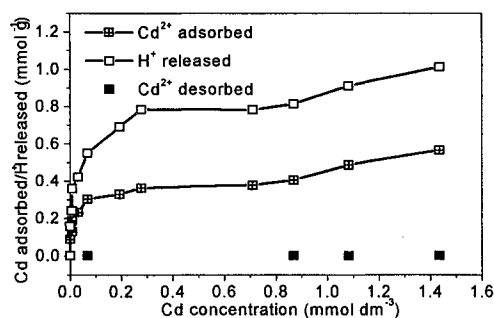


Figure 2 A comparison of the amounts of adsorbed Cd^{2+} on carbon CN with released H^+ and desorbed Cd^{2+}

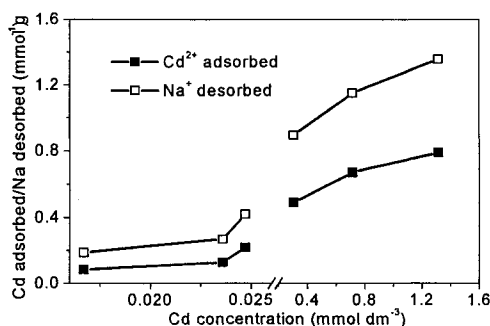


Figure 3 A comparison of the amounts of adsorbed Cd^{2+} with released Na^+ for carbon CN after reaction with NaOH

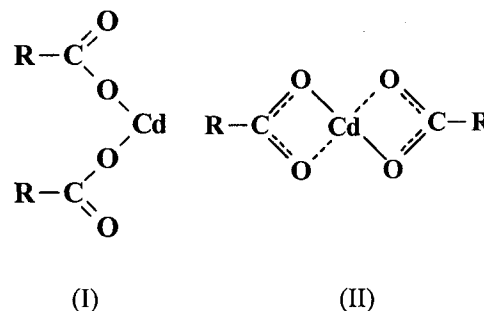


Figure 4 Possible modes of carboxylate coordination with cadmium cation