HIGH CONCENTRATION PREFERENTIAL ADSORPTION OF ZINC CHLORIDE ONTO ACID TREATED ACTIVATED CARBON AND COMPARISON TO COPPER ACETATE AND ZINC ACETATE

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Introduction

Metals like zinc and copper have conventionally been used as impregnants on activated carbon (AC) to improve its ability to remove toxic gases. The lack of scientific literature on adsorption from concentrated solutions has made us to work on the adsorption of high concentrations of zinc chloride, which was identified as a preferentially adsorbing salt [1].

Experimental

An AC imported from China (referred to as CAC in this text) was used. Nitric acid treated CAC was also used in this study and is referred to as NCAC. The nitric acid treatment was done by boiling CAC in 5 M nitric acid for 5 h and then rinsing with distilled water until the pH of the wash became close to the initial pH of distilled water.

The BET surface areas of the CAC and NCAC, determined by using a Micromeritics ASAP2020 analyzer, are given in Table 1. Boehm titration results are given in Table 2. Several solutions of linearly varying concentrations of zinc chloride were prepared. For each concentration, 4.0 g of AC was added to a vessel containing 100 mL of solution. The resulting solutions and carbon were stirred for one hour. After some time, aliquots of the solution were drawn to be analyzed for zinc concentration by atomic absorption spectroscopy (AAS).

Results and discussion

Table 1 shows that the surface area of CAC has decreased after the nitric acid treatment. This is because acid treatment attaches a large number of acidic functional groups on the surface of AC, which block some of the micropores, thus decreasing the surface area.

Table 1. BET surface areas of the AC samples (m^2/g)

CAC	NCAC
1008 ± 15	839 ± 15

It is clear from the Boehm titration results shown in Table 2 that the nitric acid treatment has imparted a very large number of functional groups to the surface of AC.

Table 2. Boehm titration results of the AC samples (mmol/g AC)

	$NaHCO_3$	Na_2CO_3	NaOH
CAC	0.0	0.0	0.07
NCAC	0.12	0.09	1.00

The adsorption data has been fitted to the Langmuir isotherm. The terms fitted to the preferential adsorption curve are shown in the following equation:

$$n = \frac{N'(C/C_0)}{\exp[(\mu_0{}^{a} - \mu_0{}^{s})/(k_B T)] + (C/C_0)} = \frac{N'C}{b+C}$$

$$b = \exp[(\mu_0{}^{a} - \mu_0{}^{s})/(k_B T)]$$

where n is the number of moles of impregnant per gram of carbon, C is the concentration of the solution used, C_o is 1M, N' is the number of moles of adsorption sites per gram of carbon and $\mu_0{}^{a}$ - $\mu_0{}^{s}$ represent the difference between the chemical potentials of adsorbed and dissolved salts in the standard state, k_B is Boltzmann's constant, and T is the temperature. In this case, N' and b were used as fitting parameters.

The data has also been fitted to the BET equation which describes adsorption with energy of interaction ϵ_1 and allows subsequent adsorption with energy of interaction ϵ_L. In the BET equation:

$$\theta = \sigma/N' = (x/\beta)/[(1 - x)(1 - x + x/\beta)]$$

where $x = C/C_o$

and $\beta = \exp\{[\epsilon_L - \epsilon_1]/kT\}$

C_o = Solubility limit of $ZnCl_2$

In this case, C_o, β and N' were used as fitting parameters.

Figure 1 and Figure 2 display the amounts of adsorbed zinc chloride against the equilibrium solution concentrations on log-log scales fitted to a sum of Langmuir and BET Isotherms for CAC for NCAC respectively. A clear plateau can be seen in the fitted curve in figure 1 pointing towards the presence of two different mechanisms of adsorption at the low and high concentrations.

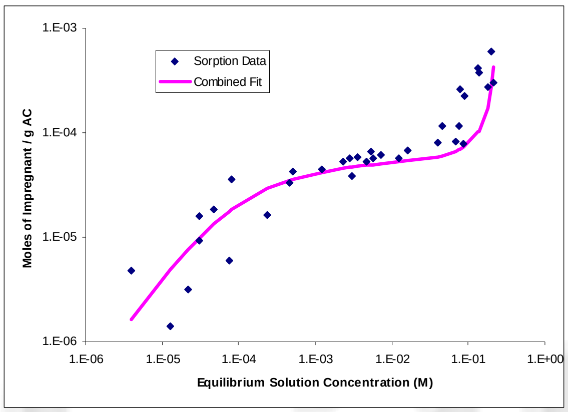

Figure 1. Adsorption Isotherm for zinc chloride on CAC, fitted to a sum of Langmuir & BET Isotherms

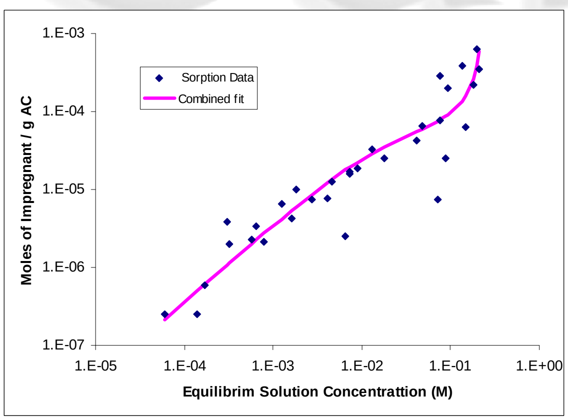

Figure 2. Adsorption Isotherm for zinc chloride on NCAC, fitted to a sum of Langmuir & BET Isotherms

Table 3 displays the values of N' and $(\mu_0^a - \mu_0^s)$/kBT for the low concentration Langmuir fitting and the values of N', $(\epsilon_L - \epsilon_1)$/kT and C_o for the high concentration BET fitting both for CAC and NCAC.

Table 3. Adsorption Parameters from Langmuir and BET Fittings.

		CAC	NCAC
Langmuir	N' (mmol/g AC)	0.02 ± 0.01	0.02 ± 0.01
	$(\mu_0^a - \mu_0^s) / (k_BT)$	-6.7 ± 0.1	-2.6 ± 0.1
BET	N' (mmol/g AC)	0.03 ± 0.01	0.06 ± 0.01
	$(\epsilon_L - \epsilon_1) / (kT)$	-7.9 ± 0.2	-2.7 ± 0.2
	C_o (mol/L)	0.23 ± 0.01	0.23 ± 0.01

It is clear that the value of N' for Langmuir fitting are much different from the N' for the BET fitting values in the case of NCAC. These very distinct values indicate that there are two different adsorption mechanisms in action at the low and high concentrations in the acid treated AC sample. The drop in the values of $(\mu_0^a - \mu_0^s)/k_BT$ and $(\epsilon_L - \epsilon_1)/kT$ in NCAC as compared to CAC is in accordance with the results obtained in [2] for copper acetate and in [3] for zinc acetate.

Conclusions

The nitric acid treatment decreased the surface area of the AC. A large range of linearly varying concentrations of aqueous zinc chloride solutions was made and stirred with each sample of CAC and NCAC. The adsorption data were fitted to a sum of Langmuir and BET isotherms. For NCAC, the BET fitting seems better than the BET fitting for the CAC. The high concentration adsorption for both carbons requires further detailed studies to develop a full picture of the impregnation science at a desired impregnant loading.

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References

[1] Westreich P, Selig S, Fortier H, Dahn JR. Two distinct Langmuir Isotherms describe the adsorption of certain salts onto activated carbon over a wide concentration range. Carbon 2006;44(14):3145-3148.

[2] Fraooq A, Westreich P, Irfan N, Dahn JR. Adsorption of copper acetate onto pretreated activated carbons over a wide concentration range. Ind. Eng. Chem. Res. 2009;48:9804-9808.

[3] Fraooq A, Mehboob S, Chaudhary MM, Irfan N. High concentration preferential adsorption of zinc acetate onto acid treated activated carbons for impregnation purposes. The Nucleus 2009;46(3):237-240.