HIGH CONCENTRATION PREFERENTIAL ADSORPTION OF ZINC ACETATE ONTO ACID TREATED ACTIVATED CARBON FOR IMPREGNATION PURPOSES

*A. FAROOQ, S. MEHBOOB, M.M. CHAUDHRY and N. IRFAN

Department of Chemical & Materials Engineering, PIEAS, P. O. Nilore, Islamabad, Pakistan

Impregnation of activated carbon has long been the subject of researchers working in the area of protection against air pollutants, especially those interested in making personal protective equipments. People who are involved in research of heavy metal removal using activated carbon have worked at very low concentrations. Moreover, the literature available in the open domain does not reveal the secrets of working at high concentration i.e., greater than 1 mM. Working at higher salt concentrations is necessary for the purpose of impregnating the activated carbon to a certain level with metals like copper, zinc, silver, chromium, tungsten, molybdenum etc. Activated carbon impregnated with these metals can be very effective in the removal of certain toxic gases. A locally available microporous activated carbon GAC89 was pretreated with nitric acid. B.E.T. surface areas and Boehm titrations were done. A large range of concentrations of aqueous solution of zinc acetate which is a preferentially adsorbing salt was made and stirred with the raw AC and the pretreated AC. Atomic absorption spectroscopy was employed to determine the amount of zinc acetate actually adsorbed onto the carbon sample. The results were fitted to a sum of two distinct adsorption isotherms, one for low concentrations i.e., less than 1 mM, and the other for high concentrations. The lower concentration adsorption is largely influenced by the solution pH. It is observed that at higher concentrations, the adsorption is weaker and the underlying mechanism is under study.

Keywords: impregnation, GAC89, Activated carbon, Boehm titrations, Adsorption

1.   Introduction

Using zinc as an impregnant improves the ability of activated carbon (AC) to remove certain toxic gases [1]. There are two commonly used methods of impregnation, the soaking method and the incipient wetness method. The soaking method involves stirring the activated carbon in an aqueous solution of a metallic salt having a particular concentration. In the second method, the amount of impregnant added is just enough to make the solution sticky. Typically, an impregnant loading of 0.1-20% by weight is required [1]. While there is much generally available literature regarding the removal of metals using activated carbon from metal solutions of concentrations below 0.1mM, there is a lack of scientific literature on adsorption from concentrated solutions. Adsorption of high concentrations of zinc acetate, which was identified as a preferentially adsorbing salt in previous work [2], has been studied on an acid treated carbon in this study.

2.   Experimental

Locally available GAC89 (referred to as AC in this text) was used. Nitric acid treated GAC89 was also used in this study and is referred to as NTAC. The nitric acid treatment [3] was done by boiling AC in 5 M nitric acid for 5 h and then rinsing with distilled water until the pH of the wash was greater than five.

The BET surface areas of the AC and NTAC, determined by using a Quantachrome 2200e gas adsorption analyzer, are given in Table 1. Boehm titration results are given in Table 2. Nineteen solutions of linearly varying concentrations of zinc acetate were prepared. For each concentration, 4.0 g of carbon (dried overnight at 120°C) was added to a vessel containing 100 mL of solution. The resulting solutions and carbon were stirred for one hour. After leaving the vessels undisturbed for 24 hours, aliquots of the solution were drawn to be analyzed for zinc concentration by atomic absorption spectroscopy (AAS).

3.   Results and Discussion

Table 1 shows that the surface area of AC 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 [3-5], thus decreasing the surface area.

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

AC	NTAC
960 ±20	850 ±20

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$_2$CO$_3$	NaOH
AC	0.01	0.01	0.08
NTAC	0.14	0.11	2.84

The adsorption data for the double Langmuir fitting has been divided into two parts, the low concentration and the high concentration data which are being called here as the Langmuir # 1 and Langmuir # 2 respectively. The Langmuir terms [2, 6] fitted to the preferential adsorption curve have been combined in equation shown below:

$$n = \frac{N_1'(C / C_0)}{\exp[(\mu_{0_1}{}^a - \mu_{0_1}{}^s)/(k_B T)] + (C / C_0)} + $$

$$\frac{N_2'(C / C_0)}{\mathrm{xp}[(\mu_{0_2}{}^a - \mu_{0_2}{}^s)/(k_B T)] + (C / C_0)} \quad (1)$$

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$_1'$ and N$_2'$ are the number of moles of adsorption sites per gram of carbon and $\mu_{01}{}^a$ - $\mu_{01}{}^s$ and $\mu_{02}{}^a$ - $\mu_{02}{}^s$ represent the difference between the chemical potentials of adsorbed and dissolved salts in the standard state for the Langmuir # 1 and Langmuir # 2 respectively, k$_B$ is Boltzmann's constant, and T is the temperature.

On the basis of the least squares curve fitting, the determination of the parameters N$_1'$ and $\mu_{01}{}^a$ - $\mu_{01}{}^s$ for the low concentration Langmuir # 1and N$_2'$ and $\mu_{02}{}^a$ - $\mu_{02}{}^s$ for the high concentration Langmuir # 2 has been performed for the AC. Whereas for the NTAC, the data has been fitted only to a single Langmuir isotherm and hence the parameters N' and $\mu_0{}^a$ - $\mu_0{}^s$ have been obtained.

Figures 1 and 2 display the amounts of adsorbed zinc acetate against the equilibrium solution concentrations on log-log scales fitted to a sum of two Langmuir Isotherms for untreated AC [2] and to a single Langmuir isotherm for the NTAC respectively. A very small 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.
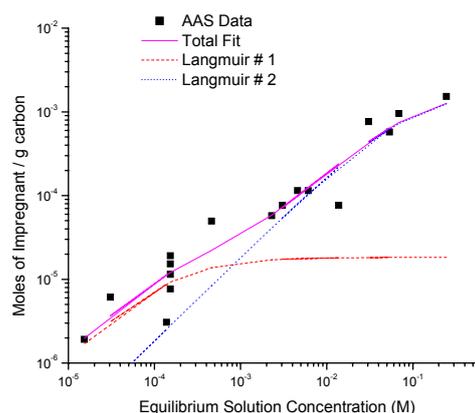

Figure 1. Adsorption Isotherm for zinc acetate on AC, fitted to a sum of two Langmuir Isotherms.
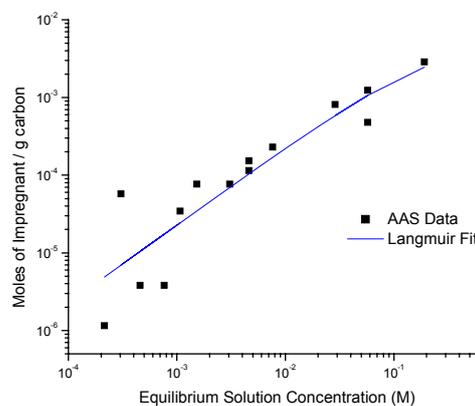

Figure 2. Adsorption Isotherm for zinc acetate on NTAC, fitted to a single Langmuir Isotherm.

Table 3 displays the values of N' and ($\mu_0{}^a$ - $\mu_0{}^s$)/k$_B$T both for the low concentration Langmuir #1 and for the high concentration Langmuir #2 determined from the data shown in Figures 1 and 2. It is clear that the values of N' and ($\mu_0{}^a$ - $\mu_0{}^s$)/k$_B$T for Langmuir #1 are much different from the respective Langmuir #2 values in the case of AC.

As already discussed in [2], these very distinct values indicate that there are two entirely different adsorption mechanisms in action at the low and high concentrations in the AC samples.

The presence of a plateau is less clear in the NTAC data (figure 2). More and better data for acid treated AC is needed before meaningful fits can be made to the data.

Table 3. Adsorption parameters from Langmuir fits.

Carbon	Langmuir # 1		Langmuir # 2	
	N' (mmol/g AC)	$(\mu_0^a - \mu_0^s) / (k_B T)$	N' (mmol/g AC)	$(\mu_0^a - \mu_0^s) / (k_B T)$
AC	0.02	-8.81	1.72	-2.36
NTAC	-	-	5.61	-1.4

It is generally understood that low concentration adsorption is caused by the interaction of functional groups present on the surface of the AC [5]. The adsorption over and above the number of functional groups present on the surface of the AC clearly cannot be attributed to interactions with acidic surface groups. A comparison of the N' values and $(\mu_0^a - \mu_0^s)/k_B T$ for Langmuir #1 for the two carbon samples in Table 3 with the same values for Langmuir #2 shows that the high concentration adsorption, which is taking place due to a much weaker interaction, cannot be attributed to the presence of functional groups on the surface of the respective carbons. One possible mechanism can be the interaction of organic acetate ions with aromatic centers on the carbon [2, 7]. Hydrolysis products of zinc acetate can also play their role in high concentration adsorption [2, 8-10].

The double Langmuir fit of Figure 1 captures the low- and high-concentration regions but for the NTAC, this fit is not applicable. Table 3 and Figure 2 show that there is some discrepancy between the number of acidic functional groups on NTAC and the N' value. A simple low concentration Langmuir isotherm would flatten out when all the acidic sites are filled, but this does not happen with the NTAC data. Figure 2 shows that the NTAC data behave differently than the AC. For the NTAC one possible explanation of this different behavior

is that a greater number of functional groups gives more possible sites for Zn^{2+} adsorption and as the Zn^{2+} is adsorbed, H^+ is released, causing the surrounding solution pH to decrease as can be seen in figure 3.
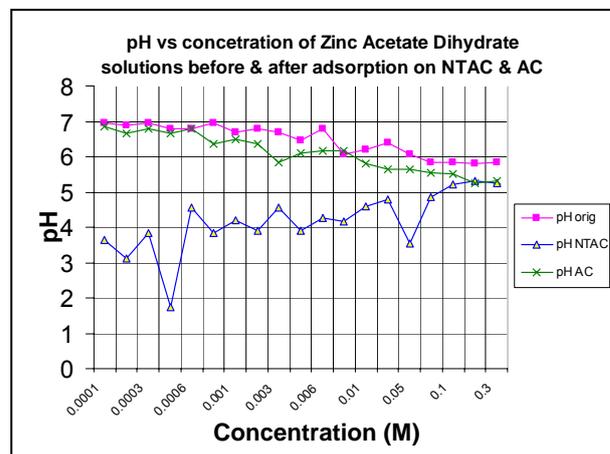

Figure 3. Variation of pH with concentration for AC and NTAC.

This increase in H^+ concentration of the solution results in a shift of the chemical potential, making it more energetically unfavourable to continue to remove H^+ from the carbon surface sites. It has also been quoted that lower metal removal occurs at lower pH values [9-15]. This is because of the dependence of dissociation of surface functional groups on the solution pH. As pH increases, more surface functional groups dissociate to provide binding sites for metal ions, thus resulting in higher adsorption [16]. At low pH, the high concentration of protons in solution competes with the metal cations for the adsorption sites, which can account for the low metal ion uptake at low pH [14, 17]. At the highest concentrations, the total adsorption of zinc acetate on NTAC resembles that of AC. Further work is needed to verify the results.

4.   Conclusions

GAC89 was pretreated with nitric acid to produce NTAC. This was done to obtain a very large number of acidic surface functional groups. B.E.T. surface area measurements and Boehm titrations were done to find the surface area and the numbers of surface functional groups for each carbon. The nitric acid treatment decreased the surface area. A large range of linearly varying concentrations of aqueous zinc acetate solutions was made and stirred with each sample of AC and

NTAC. The adsorption data were fitted to a sum of two distinct Langmuir isotherms for AC. For NTAC, there appear to be a variety of types of adsorption sites and mechanisms. The high concentration adsorption for both carbons is thought to be mainly due to adsorption on basal graphitic surfaces. Further detailed studies are needed to develop a full picture of the impregnation science at a desired impregnant loading.

References

[1] V. Bush, C.J.B and W.A. Noyes , Military problems with aerosols and nonpersistent gases. (1946) OSRD, NDRC, Division 10 Washington, D. C.

[2] P. Westreich, S. Selig, H. Fortier and J.R. Dahn, Carbon **44**, No. 14 (2006) 3145.

[3] P. Westreich, H. Fortier, S. Flynn, S. Foster, and J.R. Dahn, J. Phys. Chem. C **111**, No. 9 (2007) 3680..

[4] J.W. Shim, S.J. Park and S.K. Ryu, Carbon, **39**, No. 11 (2001) 1635.

[5] B. Xiao and K.M. Thomas, Langmuir **21**, **No.** 9 (2005) 3892.

[6] I. Langmuir, J. Am. Chem. Soc. **40**, No. 9 (1918) 1361.

[7] K.K. Bong, A.N. Nyrkova, M.M. Chobanu, G.K. Shestakov, and O.N. Temkin, Russian J. Appl. Chem. **70**, No. 12 (1997) 1872.

[8] T.K. Budinova, N.V. Petrov, V.N. Minkova, and K.M. Gergova, J. Chem. Tech. & Biotech. **60**, No. 2 (1994) 177.

[9] J.P. Chen and M.S. Lin, Water Research **35**, No. 10 (2001) 2385.

[10] A. Netzer and D.E. Hughes, Water Research, **18**, No. 8 (1984) 927.

[11] J.P. Chen, S. Yiacoumi and T.G. Blaydes, Separations Technology **6**, No. 2 (1996) 133.

[12] J.P. De Mesquita, P.B. Martelli and H.D.F. Gorgulho, Journal of the Brazilian Chemical Society, **17**, No. 6 (2006) 1133.

[13] D. Satapathy and G.S. Natarajan, Indian Journal of Chemistry Section a-Inorganic Bio-Inorganic Physical Theoretical & Analytical Chemistry, **45**, No. 9 (2006) 2011.

[14] E.Y. Kucukgul and S. Kudu, Fresenius Environmental Bulletin **15**, No. 6 (2006) 512.

[15] K.H. Chu and M.A. Hashim, J. Chem. Tech. and Biotech. **75**, No. 11 (2000) 1054.

[16] J.P. Chen, S.N. Wu and K.H. Chong, Carbon, **41**, No. 10 (2003) 1979.

[17] M.I. Kandah, Separation and Purification Technology, **35**, No. 1 (2004) 61.