Journal of Applied Sciences

ISSN 1812-5654

science alert

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Journal of Applied Sciences 10 (12): 1192-1195, 2010
ISSN 1812-5654

Metal-polyethyleneimine-activated Carbon Interaction Parameter at Equilibrium Adsorption Capacity

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Abstract: A simple interaction parameter (I_{PEI}) for adsorption of metal ions on polyethyleneimine (PEI)-impregnated activated carbon (AC) has been determined and compared. It is used to elucidate and compare the degree of interaction between metal and surface of PEI-impregnated AC.

Key words: Polyethyleneimine, activated carbon, metal ions

INTRODUCTION

Adsorption using Activated Carbon (AC) is frequently used to 'polish' industrial effluent prior to ultimate discharge into the environment. Recent research has focused on chemical modification of AC to improve metal affinity and/or increase the activated carbon's affinity towards certain metal species. One frequently used modification technique was via wet oxidization using strong acid solutions (Jia and Thomas, 2000; Park and Jang, 2002; Strelko and Malik, 2002) to increase metal affinity.

We have previously investigated the effects of polyethyleneimine (PEI) impregnation amount and types of PEI used on surface characteristics as well as metal ions adsorption capacities of palm shell AC (Yin *et al*., 2008). PEI is a well-recognized polymer with high metal chelation capability, high content of functional groups, good water solubility and chemical stability (Juang and Chen, 1996). We determine that impregnation at 8.41 wt.% 423 PEI/AC provides optimum increases for nickel and copper adsorption capacities by factors of 2.6 and 1.5, respectively at 49% reduction of Brunauer-Emmett-Teller (BET) surface area as compared to virgin AC. We also show that only 423-PEI molecules have considerably filled the micropores of AC whereas the 600- and 1200-PEI molecules are too large (in terms of molecular sizes) to infiltrate the micropores.

To further elucidate the effect of PEI impregnation amount on equilibrium adsorption capacity of metal ions on AC, an interaction parameter (designated as I_{PEI}) for adsorption of heavy metal ions on PEI impregnated AC has been calculated and compared in this paper. It should be noted that I_{PEI} is not equivalent to a complexation constant and it is only calculated to compare the degree of interaction between heavy metal and surface of PEI-impregnated AC.

MATERIALS AND METHODS

The AC used was palm shell-based and produced by physical activation process with steam as the activating agent. It was supplied by Bravo Green Sdn Bhd (Malaysia). PEI impregnation and physical characterization of palm shell AC samples was conducted in our previous work (Yin *et al*., 2008). The surface morphology of the AC was analysed using Phillips XL 30 electron microscope.

RESULTS AND DISCUSSION

Textural characteristics: Table 1 shows the textural characteristics of virgin and PEI-impregnated AC samples. It was determined that the impregnation percentages for PEI surface saturation for 423, 600 and 1200-PEI are 29.82, 8.26 and 3.92 wt.% PEI/AC, respectively. The increase of percentage PEI impregnation reduces the BET surface area for a particular type of PEI implying that higher quantity of PEI in bulk solution promotes higher adsorption on the surface of the AC resulting in decrease of free surface area. Figure 1a and b show the SEM micrographs of the virgin and PEI-impregnated AC. Pores of virgin sample distributed across its surface are slit-shaped, an aspect dissimilar to the general honeycomb

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Table 1: Textural characteristics of virgin and PEI-impregnated activated carbon

Type of PEI	Percentage impregnation (wt.% PEI/AC)	BET surface area ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	Average pore diameter (nm)	Porosity (%)	
					Micro(<2 nm)	Meso(>2 nm)
	Virgin	1027	0.4501	1.75	96.58	3.42
423-PEI	4.76	777	0.364	1.87	90.49	9.51
	8.41	532	0.2687	2.02	87.94	12.06
	16.68	128	0.0966	3.03	63.83	36.17
	29.82	33	0.0254	3.06	70.78	29.22
600-PEI	3.10	817	0.3563	1.74	95.40	4.60
	4.51	736	0.325	1.77	94.77	5.23
	7.69	683	0.3036	1.78	93.45	6.55
	8.26	626	0.2991	1.91	87.40	12.60
1200-PEI	1.40	987	0.43	1.74	95.77	4.23
	2.08	924	0.4051	1.75	95.58	4.42
	3.54	831	0.3605	1.74	96.01	3.99
	3.92	783	0.3405	1.74	96.45	3.55

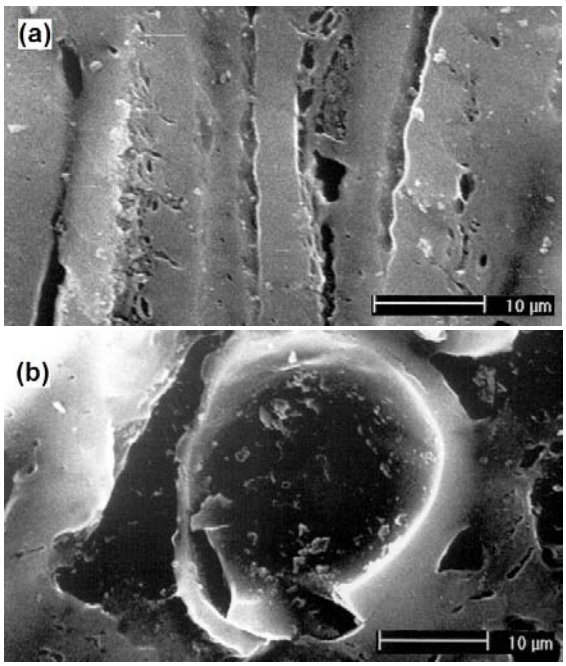

Fig. 1: SEM micrographs of (a) virgin AC and (b) PEI-impregnated AC

or circular pores normally present in other agricultural material-based Acs (Tseng *et al*., 2006). It is suggested that these slit shaped pores inhibit the adsorption of 1200-PEI molecules which was too large to infiltrate them (Yin *et al*., 2007).

Interaction parameter: The general equilibrium equation for interaction/adsorption of M^{2+} ions with PEI on surface of AC and I_{PEI} are represented by:

$$PEI+M^{2+} \rightleftharpoons PEI\text{-}M^{2+} \quad (1)$$

$$I_{PEI} = \frac{\left[PEI - m^{2+}\right]}{[PEI]^{*}\left[M^{2+}\right]} \quad (2)$$

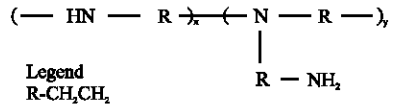

Fig. 2: General polyethyleneimine structure (Sigma)

To simplify calculation of the I_{PEI} values, assumptions are made based on schematic model on complexes formed between Cu^{2+} and PEI as created by Molochnikov *et al*. (2003). They reported that most of the nitrogen atoms along one PEI chain are protonated in acidic solutions. They further added that the probability of deprotonation for two adjacent nitrogens in one chain is very low. Hence, copper complexes formed under acidic conditions, most likely, include only nitrogen atoms of different polymeric chains or, in some cases, nitrogen atoms positioned far from each other along one chain. They based their schematic model on the complexation reactions between four secondary amines (-NH-) and one Cu^{2+} ion.

Based on Fig. 2 which illustrates the general structure of polyethyleneimine and the three types of PEI, their molecular structures for determination of I_{PEI} have been proposed (Fig. 3). From Fig. 3a-c, the amounts of amine groups in one molecule of 423-PEI, 600-PEI and 1200-PEI are determined to be 10, 14 and 28, respectively. Therefore, in order to provide an estimation of the I_{PEI} values, two Cu^{2+} ions are assumed, based on Molochnikov *et al*. (2003) model, to form a complex with one 423-PEI molecule. Also, three and seven Cu^{2+} ions are assumed to form a complex each, with a 600 and 1200-PEI molecule respectively. For this calculation, it is also assumed that all Cu^{2+} ions react entirely with PEI molecules. For Eq. 1 and 2, [PEI] and $[M^{2+}]$ represent remaining equilibrium PEI (unreacted) and Cu^{2+} or Ni^{2+} (free ions) concentrations on surface respectively and they are estimated based on simple mass balance calculations. To ensure brevity and simplicity of the I_{PEI}

Table 2: Comparison of I_{PEI} values for Cu^{2+} and Ni^{2+} for PEI-impregnated AC

	$M^{2+} = Cu^{2+}$				$M^{2+} = Ni^{2+}$			
PEI-impregnated AC	[PEI-M^{2+}] (mmol L^{-1})	[PEI] (mmol L^{-1})	[M^{2+}] (mmol L^{-1})	IPEI (mmol L^{-1})	[PEI-M^{2+}] (mmol L^{-1})	[PEI] (mmol L^{-1})	[M^{2+}] (mmol L^{-1})	IPEI (mmol L^{-1})
4.76 wt.% 423-PEI/AC	0.685	-0.103	1.631	-4.064	0.223	0.359	2.555	0.243
8.41 wt.% 423-PEI/AC	0.861	0.207	1.279	3.253	0.505	0.562	1.99	0.452
16.68 wt.% 423-PEI/AC	0.74	1.588	1.521	0.306	0.4	1.927	2.199	0.094
29.82 wt.% 423-PEI/AC	0.661	4.28	1.678	0.092	0.303	4.638	2.395	0.027
3.10 wt.% 600-PEI/AC	0.4144	-0.1495	1.7569	-1.5772	0.144	0.1209	2.5681	0.4639
4.51 wt.% 600-PEI/AC	0.3777	0.0133	1.867	15.183	0.1598	0.2312	2.5207	0.2741
7.69 wt.% 600-PEI/AC	0.4039	0.2857	1.7884	0.7904	0.1941	0.4955	2.4176	0.1621
8.26 wt.% 600-PEI/AC	0.4545	0.2909	1.6366	0.9547	0.2002	0.5452	2.3995	0.153
1.40 wt.% 1200-PEI/AC	0.1506	-0.0917	1.9457	-0.8437	0.0578	0.001	2.5952	21.5741
2.08 wt.% 1200-PEI/AC	0.1484	-0.0603	1.9615	-1.2545	0.0558	0.0323	2.6093	0.6632
3.54 wt.% 1200-PEI/AC	0.1259	0.0263	2.1188	2.2619	0.0523	0.0999	2.6342	0.1986
3.92 wt.% 1200-PEI/AC	0.1371	0.032	2.0401	2.0987	0.0465	0.1227	2.6746	0.1417

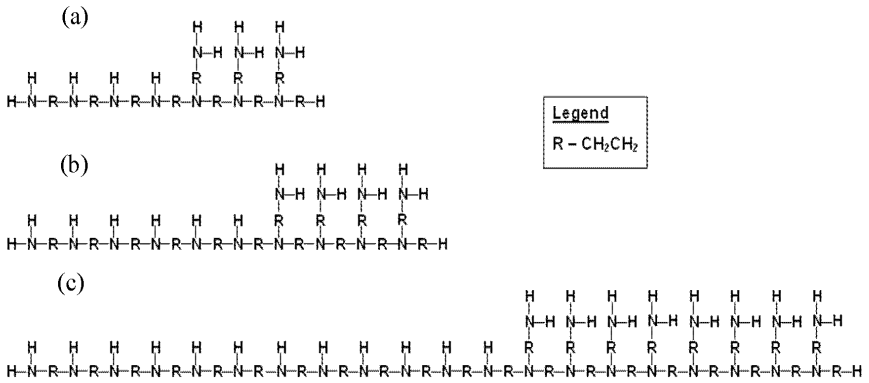

Fig. 3: Proposed (a) 423, (b) 600 and (c) 1200-PEI molecular structures used for determination of I_{PEI}

values for Ni^{2+} were also calculated based on the method used to calculation the I_{PEI} values for Cu^{2+}. Table 2 compares the determined I_{PEI} values for both Cu^{2+} and Ni^{2+} for PEI impregnated AC. It is obvious that 8.41 wt.% 423-PEI/AC has the highest [PEI-Cu^{2+}] values forv both Cu^{2+} and Ni^{2+} at 3.253 and 0.452 mmol L^{-1}, respectively. This indicates that the surface 8.41 wt.% 423-PEI/AC has the highest concentrations of PEI-Cu^{2+} and PEI-Ni^{2+} complexes as compared to the other PEI-impregnated AC. This is in good agreement with the results described in Section 4.3.4. The negative values of [PEI] and I_{PEI} observed for 4.76 wt.% 423-PEI/AC, 3.10 wt.% 600-PEI/AC, 1.40 wt.% 1200-PEI/AC and 2.08 wt.% 1200-PEI/AC provide indication of insufficient quantity of PEI molecules on surface of AC needed to enable significant complexation reactions. The calculated I_{PEI} values present a rather interesting result as they seem to vary for different types of wt.%, PEI types and metal ions. For adsorption of Cu^{2+}, I_{PEI} values are observed to be highest for 8.41 wt.% 423-PEI/AC, 4.51 wt.% 600-PEI/AC and 3.54 wt.% 1200-PEI/AC. This shows that the degree of interaction (which ultimately leads to complexation) between Cu^{2+} and PEI on surface of these AC samples is the highest for each type of PEI. This is due to the optimum presence of PEI molecules on the surface of AC which are sufficient in quantity for contact with Cu^{2+} and yet reduction of cumulative pore volume is minimized.

CONCLUSIONS

A simple interaction parameter (I_{PEI}) for adsorption of metal ions on polyethyleneimine (PEI)-impregnated activated carbon (AC) has been determined and compared. The calculated I_{PEI} values present a rather interesting result as they vary for different types of wt.%, PEI types and metal ions. This parameter can be used to quantify the degree of interaction between functional groups present in a porous materials and metal ions.

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