REMOVAL OF IONIC LIQUIDS AND METHYLENE BLUE USING VARIOUS ACTIVATED CARBONS

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Introduction

Ionic liquids (ILs) being soluble in water pose a serious threat to the environment and their toxicity has also been reported. Only few works were focused on ILs removal through AC and a previous work based on imidazolium type ILs did not show appreciable results regarding AC [1]. A very recent detailed investigation for adsorption of imidazolium based ILs onto AC has reported the effects of cations, anions and surface chemistry on the adsorption efficiency [2]. Another issue which the environmentalists have been trying to tackle for the last many years is the removal of dyes from the waste stream of a processing/dyeing industry. The present work aims at investigating the adsorption profile and uptake of various ILs on three activated carbons coming from different origins which differ in terms of porous texture and surface chemistry. Methylene blue being a typical cationic dye was selected to compare its adsorption with the selected ILs.

Experimental

The three types of ionic liquids used were 1-methyl 3-octylimidazolium chloride (OMImCl), 1-butyl 3-methylimidazolium chloride (BMImCl) and octylpyridinium bromide (OPyBr). OMImCl was synthesized in our laboratory using microwave irradiation, OPyBr was also synthesized in our laboratory, whereas BMImCl and Methylene Blue (M Blue) were obtained commercially. The three activated carbons (AC) were, a microporous coal based granulated AC from China, a mesoporous AC fabric from Calgon and an AC prepared from artichokes using phosphoric acid activation (called Chinese AC, Fabric AC and Artichokes AC respectively).

The adsorption experiments were all performed at 25°C by stirring stoppered 100 mL flasks containing the suspensions of AC in ILs solutions on a magnetic stirring plate. The ionic liquids and dye adsorption kinetics and isotherms on the ACs were studied using UV-Visible spectrometry. All the isotherms were obtained under controlled pH conditions in buffer solutions at pH 2, 7 and 9. A 50 mL volume of the adsorbate solution made in the buffer was stirred with weighted amounts of AC in each case (0.1 g for the Chinese AC and 0.05 g each for the Fabric AC and the Artichokes AC). The maximum absorbance was obtained at 665 nm for M Blue, 211 nm for OMImCl and BMImCl and at 260 nm for OPyBr.

Results and Discussion

Table 1 shows the results of the "Boehm" titrations which give the semi-quantitative value of oxygenated acidic and basic functional groups on the surfaces of the respective ACs. The Chinese AC has the least amount of acidic functional groups, whereas the Artichokes AC has the most.

Table 1. Boehm titration results of three AC samples (meq.g^{-1} AC)

Activated Carbon	Carboxylic Groups (meq.g^{-1})	Lactonic Groups (meq.g^{-1})	Phenolic Groups (meq.g^{-1})	Carbonyl Groups (meq.g^{-1})	Total Basic Groups (meq.g^{-1})
Chinese AC	0	0	0.07	-	-
Fabric AC	0	0.4	0.2	0	0.1
Artichokes AC	0.46	0.68	0.38	0.44	-

The BET surface areas of the AC adsorbents, determined by using a Micromeritics ASAP2010 are shown in Table 2. The Artichokes AC has the largest surface area most of which is present as an external surface area. The Chinese AC, on the other hand is mainly microporous and the Fabric AC is mainly mesoporous.

Table 2. Surface areas and pH_{PZC} of three AC samples

Activated Carbon	BET Surface Area (m^2/g)	External Surface Area (m^2/g)	Micropore Area (t-plot) (m^2/g)	Micropore Volume (t-plot) (cm^3/g)	pH_{PZC}
Chinese AC	1205	632	573	0.25	9.5
Fabric AC	1769	376	-	0.25	6.8
Artichokes AC	2160	2010	156	0.043	6.0

Figure 1 shows the adsorption data at pH 2 and 9 for OPyBr onto the three AC samples. The effect of changing pH on the adsorption uptake is more pronounced in Artichokes AC. The highest sensitivity of the adsorption of this carbon to the pH variation is related to its surface chemistry which is very rich in acidic groups. At pH 2, the uptake is always less than at pH 9 due to the repulsion between the positively charged IL cation and the AC surface. Curves at pH 9 have a sharp knee as compared to the curves at pH 2 signifying a stronger interaction due to electrostatic attraction leading to a higher adsorption uptake.

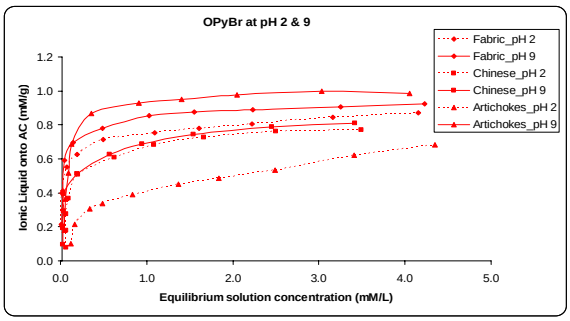

Fig. 1 Adsorption isotherms at pH 2 & 9 and 25°C for OPyBr on the Fabric, Chinese & Artichokes ACs

Figure 2 shows the adsorption isotherms at pH 9 and 25°C for the three ILs onto the three AC samples. Artichokes AC generally has higher uptake than Chinese & Fabric ACs owing to its higher BET surface area. Type of isotherms according to Giles classification [3] is H type for OPyBr as the knee is clearly visible and L type for OMImCl and BMImCl.

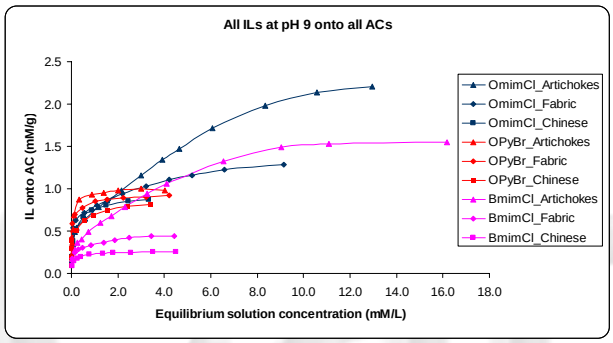

Fig. 2 Adsorption isotherms at pH 9 for OMImCl, OPyBr & BMImCl on the Fabric, Chinese & Artichokes ACs

Figure 3 shows the comparison of the adsorption isotherms at pH 7 for the three ILs onto the three AC samples. BMImCl generally is adsorbed at a lower uptake than OMImCl & OPyBr. This can be explained by the smaller chain length of BMImCl thus increasing hydrophilicity and in turn reducing the adsorption uptake [2].

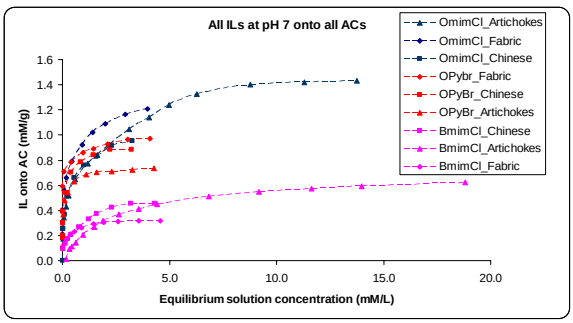

Fig. 3 Adsorption isotherms at pH 7 and 25°C for OMImCl, OPyBr & BMImCl on the Fabric, Chinese & Artichokes ACs

Figure 4 shows the adsorption isotherms at pH 7 and 9 for M Blue onto the three AC samples. The isotherms are L-type [3] and the M Blue uptake is in the order of increasing surface area of the ACs. Increasing the pH from 7 to 9 slightly reduces the adsorption uptake of M Blue contrary to what is commonly expected for this cationic dye. This decrease in adsorption uptake is smaller for the acidic Artichokes AC but higher for the more basic ACs. This suggests reduction in adsorption uptake as shifting the pH from 7 to 9 is related to the surface chemistry of the carbon which favors the adsorption at neutral pH by dispersive interactions between the delocalized π electrons on the surface of the basic activated carbons and the free electrons of the dye molecule present in the aromatic rings (and multiple bonds) [4].

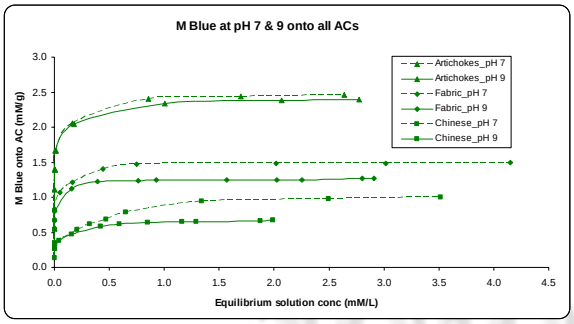

Fig. 4 Adsorption isotherms at pH 7 & 9 for M Blue on the Fabric, Chinese & Artichokes ACs.

Conclusions

Type of AC, pH, chain length and the type of IL, were found to have significant effects on the amount of adsorbent uptake. The comparison of the sizes and volumes of the studied ILs molecules and the porous volume of ACs have suggested that the ILs were mainly adsorbed in the micropore volumes. The higher uptakes for OPyBr and OMImCl compared to BMImCl were in agreement with the higher hydrophobicity of these molecules. According to the isotherms profiles, OPyBr adsorption appeared to be more energetic compared to BMImCl or OMImCl.

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References

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