

ACTIVATED CARBONS EMPLOYED TO REMOVE IONIC LIQUIDS FROM AQUEOUS SOLUTIONS

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Imidazolium and pyridinium based ionic liquids (ILs) have been separated from aqueous solutions by adsorption using a raw Chinese activated carbon (CAC), a bleached Chinese activated carbon (BAC) and an acid treated Chinese activated carbon (AAC) as adsorbent. Adsorption isotherms data of ionic liquids on activated carbons has been obtained. The influence of both cations and anions was analyzed by studying three different ILs. The role of surface chemistry of the adsorbent was also examined using activated carbons modified by oxidative treatments. The BET surface area of activated carbons was measured by nitrogen adsorption. The results of this work indicate that activated carbon is an attractive adsorbent to remove ionic liquids from water streams. It has also been demonstrated that the adsorption of hydrophilic ionic liquids can be improved by modifying the amount and nature of oxygen groups on the activated carbon surface specially by increasing basic groups. The adsorption data for isotherms was studied at acidic, neutral and basic pH values.

Keywords: Activated carbon, Adsorption, Ionic liquids, Kinetic equilibrium, Isotherms, UV visible

1. Introduction

It was initially claimed that the ionic liquids (ILs) are potentially environment friendly. However, it was later reported that they may play some role to increase the environmental pollution [1]. In reaction and separation processes, ILs have been extensively examined as an alternative to conventional organic solvents [2, 3]. Ionic liquids have many attractive properties like they have high chemical stability, low vapour pressure and are non-flammable [4]. Usually, the structure of ILs is based on imidazolium and pyridinium based cations paired with variety of inorganic and organic anions. Various cations and anions can be used in ILs to achieve desirable properties. By varying the length of alkyl chain and the hydrophilic/hydrophobic nature of the anion, the solubility of ILs in water can be modified to large extent. The applications of ILs in industry have been recently reported, some of them involving water streams in the process [5]. The synthesis of ILs includes aqueous media [6] generating wastewaters which would demand adequate solutions. The use of adsorption for such treatments has been done since long and activated carbon (AC) has been the

most common and successful adsorbent [7, 8]. A recent investigation on the effects of cations, anions and surface chemistry on the adsorption efficiency for adsorption of imidazolium based ILs onto AC has been reported [9].

This work aims at investigating the adsorption profile of various raw and treated activated carbons to test various imidazolium and pyridinium based ILs on each of the selected ACs. The ACs included: raw Chinese activated carbon (CAC) from a commercial source, bleached Chinese activated carbon (BAC) and acid treated Chinese activated carbon (AAC). Three ionic liquids 1-methyl 3-octylimidazolium chloride (OMImCl), 1-butyl-3-methylimidazolium chloride (BMImCl), and octylpyridinium bromide (OPyBr) were chosen in order to test the effect of mostly used various cations and anions. The imidazolium and pyridinium as cations and chloride and bromide were chosen as the anions. Length of the alkyl chain was also varied by using methyl, butyl and octyl. All the isotherms were studied at acidic, neutral and basic pH values.

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2. Experimental

Three types of ionic liquids used were: 1-methyl 3-octylimidazolium chloride (OMImCl), 1-butyl 3-methylimidazolium chloride (BMImCl), and octylpyridinium bromide (OPyBr). The OMImCl was synthesized in our laboratory using microwave irradiation [10], OPyBr was also synthesized in our laboratory by usual synthesis method, whereas BMImCl was supplied by Solvionic. Prior to use, the commercially obtained Chinese AC was dried in oven at 110° C and was stored in an air tight container.

Raw Chinese AC was bleached with 10% commercial grade NaOCl solution by stirring for 24 hrs at room temperature. After oxidation, the suspension was washed first with HCl for 24 hours then with distilled water for 11 days in a soxhlet extractor. The bleached AC was later filtered and dried in an oven at 110° C. The raw Chinese AC was also treated with 5 M HNO₃ by boiling for 5 hours. The treated AC was later filtered and dried in an oven after 7 days of washing in a soxhlet extractor.

The BET surface areas of the AC adsorbents were determined by using a Micromeritics instrument ASAP2020. Nitrogen was used for adsorption-desorption experiments. The values of the surface areas and micropore volumes are given Table 1.

Ten samples of each IL of same concentration were run on each of activated carbon of same weight for different time intervals to get the adsorption equilibrium time. At the equilibrium time, the rate of IL adsorption or desorption were equal and at that time the Plateau was achieved on kinetics curve. The samples were stirred for at least 24 hours duration. Each ionic liquid had its own adsorption equilibrium time for a specific activated carbon.

All of the adsorption data were obtained at room temperature and under controlled pH conditions in buffer solutions of pH 2, 7 and 9. Stopped 100 mL flasks containing the suspensions of 0.1 g AC in 50 mL ILs solutions were stirred on a magnetic stirring plate. The adsorption kinetics and isotherms on the ACs were studied using UV-Visible spectroscopy (OPTIZEN-3220). The maximum absorbance was obtained at 211 nm for OMImCl and BMImCl and at 260 nm for OPyBr.

Isotherms were studied at constant temperature on same weight of carbon by varying the concentration of ILs and stirring the sample for respective equilibrium time calculated from Kinetics. Isotherm study should continue till the Plateau has been achieved. The kinetics were studied at neutral pH only in distilled water. For the isotherms study, the buffer solutions were made by mixing 25 ml of 0.2 molar potassium chloride and 6.5 ml of 0.2 molar hydrochloric acid for pH 2, 50 ml of 0.1 molar tris(hydroxymethyl)-aminomethane and 46.6 ml of 0.1 molar hydrochloric acid for pH 7 and 50 ml of 0.025 molar disodium tetraborate decahydrate (borax) and 4.6 ml of 0.1 molar hydrochloric acid for pH 9. pH was measured by using a pH meter of Hanna Instruments HI8314.

3. Result and Discussion

The BET surface area and pore volumes of raw Chinese, bleached and acidified ACs are presented in Table 1. The bleached AC and acidified AC have lower surface area than that of the raw activated carbon. It is clear from the table that after acidification the area of the raw Chinese activated carbon has decreased because of the attachment of functional groups on its surface and blocking of some pores. The bleached AC surface area has decreased to a value half of the raw AC area showing that the treatment of the carbon has surely blocked some of the micropores. Table 1 also shows a decrease in the carbon micropore volume in the case of bleached activated carbon (BAC) and acidified activated carbon (AAC) again due to blocking of some of the micropores [12].

Table 1: Surface area and micropore volume of raw, bleached and acid treated Chinese ACs.

Activated Carbon	BET Surface Area (m ² /g)	Micropore Volume (t-plot)(cm ³ /g)
Raw Chinese AC (CAC)	1205	0.21
Bleached Chinese AC (BAC)	660	0.14
Acid Treated Chinese AC (AAC)	923	0.19

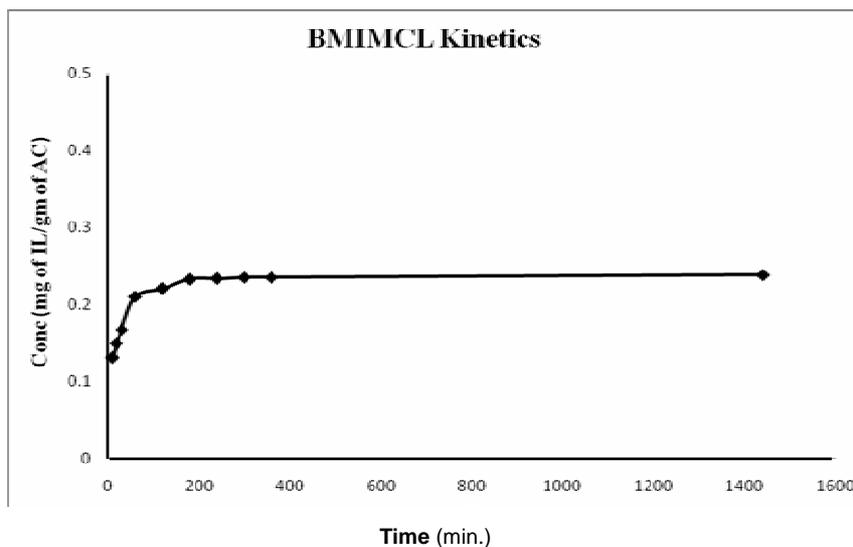


Figure 1. Kinetics curve for adsorption of BMImCl on raw Chinese activated carbon (RAC).

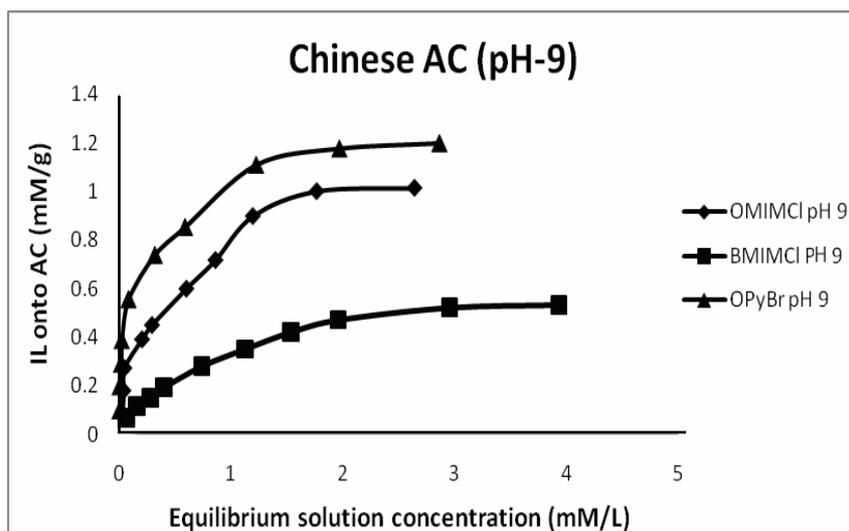


Figure 2. Experimental adsorption equilibrium data for the adsorption of OMImCl, BMImCl and OPyBr onto raw Chinese AC at pH 9.

Plateau achieved on kinetics curve in Fig. 1 for the adsorption of BMImCl on raw Chinese activated carbon shows the achievement of equilibrium and thus the minimum time to run other experiments with same combination. This is a typical curve and similar ones were obtained for other combinations of ILs and ACs. Adsorption Equilibrium time was taken as 30 hours for OMImCl and OPyBr while for BMImCl, 12 hours was selected on the basis of their respective kinetics curves on each AC. The experimental adsorption isotherms data of

OMImCl, BMImCl and OPyBr onto the raw Chinese AC at pH 9 have been shown in Fig. 2. It is clear that OPyBr has the maximum adsorption while BMImCl has the least. OMImCl curve lies close to the OpyBr curve. OPyBr and OMImCl exhibit more adsorption than BMImCl owing to their longer alkyl chain length i.e., the octyl as compared to the butyl in BMImCl. It has been reported that longer the alkyl chain length, more will be the hydrophobicity and thus more adsorption [9].

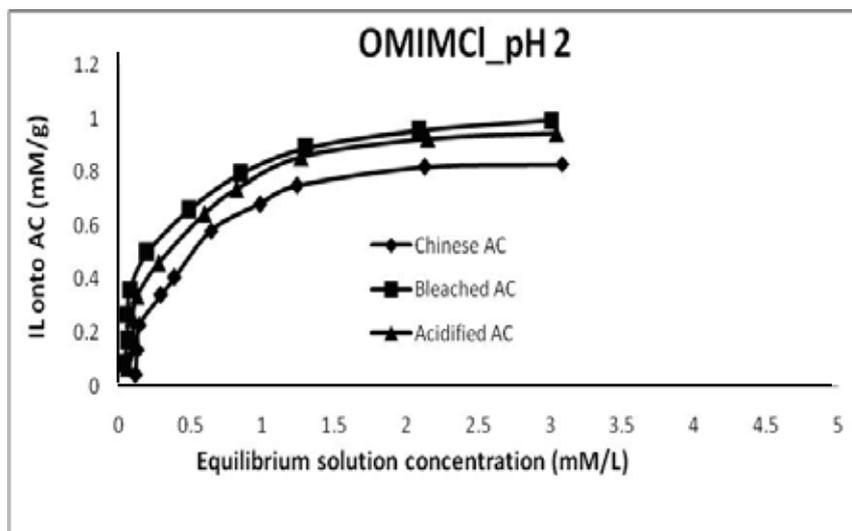


Figure 3. Experimental equilibrium data for the adsorption of OMIMCl on raw Chinese AC, bleached AC and acid treated Chinese AC at pH 2.

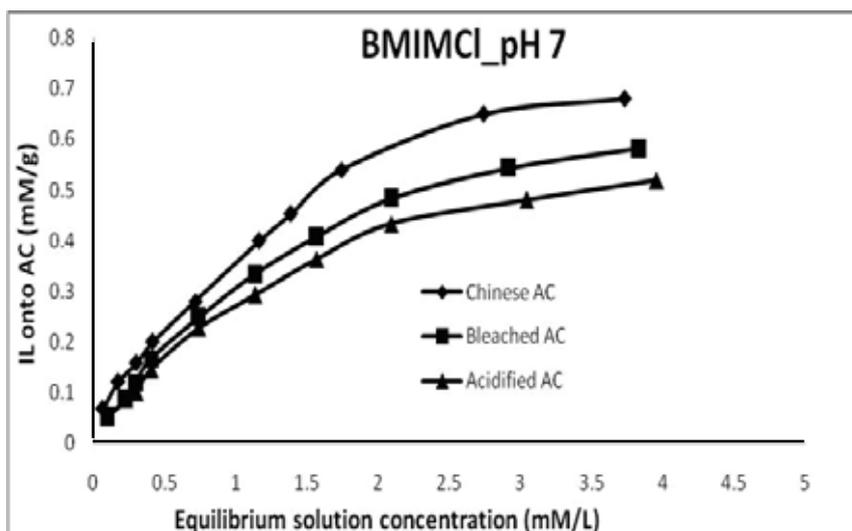


Figure 4. Experimental equilibrium data for the adsorption of BMIMCl on raw Chinese AC, bleached AC and acid treated chinese AC at pH 7.

Figure 3 shows the adsorption curves for OMIMCl at pH 2 onto all the three ACs. The experimental data obtained in the adsorption runs conducted with each ionic liquid for different activated carbons clearly shows that the adsorption capacity of bleached Chinese activated carbon is higher as compared to that of the raw Chinese activated carbon and acid treated activated carbon as shown in Fig. 3. The curves in this case are less

far apart as compared to the same curves at pH 7 and 9.

Figure 4 shows the adsorption curves for BMIMCl at pH 7 onto all the three ACs. The flat shape of the adsorption isotherms shown in Fig. 4 suggests that there is no strong interaction between the IL and the AC surface to occupy the adsorption sites. The affinity of IL for AC should be the result of several sorption mechanisms [11].

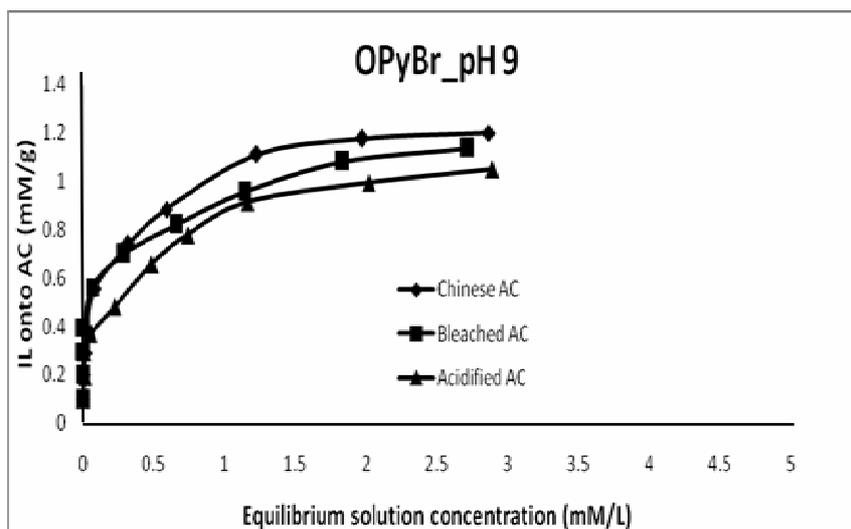


Figure 5. Experimental equilibrium data for the adsorption of OPyBr on raw Chinese AC, bleached AC and acid treated chinese AC at pH 9.

Figure 5 shows the adsorption curves for OPyBr at pH 9 onto all the three ACs. The shape of the curves having a knee exhibits strong adsorbant-adsorbate interaction. The comparison of the curves in Figs. 3-5 show that significant increase in adsorption capacity is observed as we move from acidic towards basic pH values of solution. The positive surface of carbons and the increasing electrostatic repulsion between organic cations is the probable reason of more adsorption at basic pH values. The stronger electrostatic repulsion makes the knee on the adsorption isotherms at pH=9 sharper than the knee at pH=2 or 7 isotherms. It is clear that OPyBr and OMImCl can be effectively separated by adsorption with Chinese ACs provided that they are composed of hydrophobic anions like BF_4 , PF_6 , ClO_4 etc.

4. Conclusions

The influence of the surface chemistry of activated carbon on ionic liquids adsorption was analyzed. Three Activated Carbons with different surface compositions; Raw Chinese Activated Carbon, Bleached Chinese Activated Carbon and Acidified Chinese Activated Carbon were examined by characterization and equilibrium adsorption experiments. Type and treatment of Activated Carbon, pH, chain length and the type of IL have significant effects on the amount of adsorbent uptake. The higher uptakes for octylpyridinium bromide (OPyBr) and 1-methyl 3-octylimidazolium chloride (OMImCl) compared to 1-butyl 3-methylimidazolium chloride (BMImCl) are in

agreement with the higher hydrophobicity of these molecules.

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