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Adsorption of imidazolium-based ionic liquids with different chemical structures onto various resins from aqueous solutions

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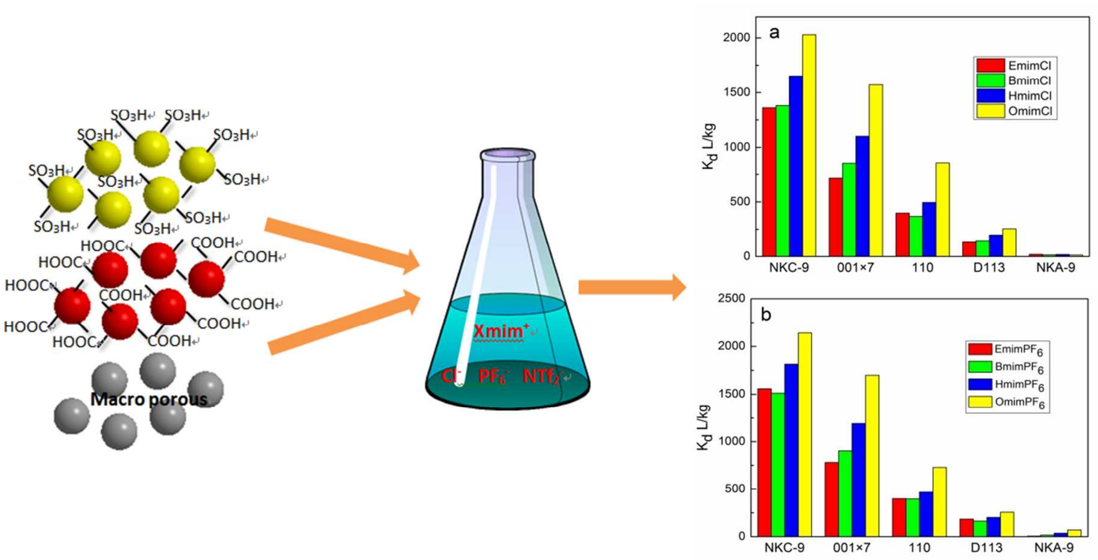
The adsorption behavior of a series of imidazolium-based ionic liquids with different chemical structures onto various resins was investigated.



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The increasing applications of ionic liquids (ILs) in many fields have led to significant attentions for their treatment before they enter the environment to prevent their potential environmental risk. In this work, a series of imidazolium-based ionic liquids with different chemical structures were selected to study their adsorption onto various resins from aqueous solutions. The results showed that the functional groups in the resin played predominant role for the adsorption of the ionic liquids onto the resins, and the adsorption capacity of the resins for the ILs decreased following a sequence of sulfonic acid > carboxylic acid > without any functional groups. The variation of the anion of ILs had slight effect on the adsorption capacity of the ILs onto the resins, but the adsorption capacity increased with increasing alkyl chain length of the imidazolium cation. The results provide an understanding of the adsorption behavior of various ILs onto different resins, and guide the removal, separation and/or recovery of different ILs from aqueous streams by resins or other sorbents.

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1. INTRODUCTION

Ionic liquids (ILs) are organic salts that have low melting points (ca. <100°C) and are typically composed of an organic cation and an inorganic anions[1]. The large variation of possible cations that can be selected for use with a given anion allows one to choose their combination for a desired property or characteristic[2]. ILs can have high solvent capacity[3], specific catalytic functions[4], generally good chemical and thermal stability[5], wide electrochemical window[6] and negligible vapor pressure[7]. Thus, ILs are being widely studied in many fields for application in synthesis, catalysis, adsorption, biofuels and energy storage[8-11]. However, the wide applications of such a diverse group of chemicals pose a risk to the environment since their release into the environment does have harmful effects on living things[12-15]. Therefore, the removal or recovery of ionic liquids from waste streams is an important process that must be studied before practical use of the IL can truly be considered as safe.

Techniques such as biodegradation[16], advanced oxidation[17, 18], distillation[19], membrane-based filtration[20], and adsorption[21, 22] have been reported for the treatment of ILs from aqueous streams. Among these techniques, adsorption is considered to be one of the most efficient and non-destructive methods to remove or recover ILs from waste streams. Different adsorbents such as montmorillonite[23], kaolinite[24], ion-exchange resin[25], and activated carbon[22] have been evaluated for the removal of ionic liquids. In these studies, montmorillonite and kaolinite exhibit limited adsorption capacity for ionic liquids, while activated carbon is highly efficient for the removal of ionic liquids from aqueous waste streams although its adsorption capacity for a given ionic liquid depends on the surface chemistry of the activated carbon. Lemus et al. investigated the adsorption of ILs onto activated carbons, and concluded that it is the surface chemistry of the ACs and the hydrophobic/hydrophilic nature of the ions of the ILs that determine the adsorption capacity of the activated carbon[26-29]. For example, common commercial activated carbons show good adsorption capacity for hydrophobic ionic liquids such as those with $[NTf_2]^-$ and $[PF_6]^-$ anions, but exhibit low adsorption capacity for hydrophilic ionic liquids such as those with Br^-, Cl^- anions[22, 26, 27]. By increasing the content of polar oxygenated groups on the activated carbon, adsorption of ionic liquids that contain hydrophilic cations or anions can be greatly improved[30].

Ion exchange resins have been broadly used in wastewater treatment, and they have also been used as efficient adsorbents for the purification or recovery of ionic liquids in their synthesis and application[31-33]. However, few research works have been carried out on the adsorption of ILs by ion exchange resins from aqueous streams for the purpose of waste treatment. Sun et al. evaluated the adsorption of 1-ethyl-3-methylimidazolium acetate ([EMIM][OAc]) onto twelve different ion-exchange resins with different functional groups from aqueous solutions, and found that the uptake of [EMIM][OAc] was dependent on the types of the active groups on the resin, while the bead size and cross-linking degree was less important in the adsorption performance[25]. Since there are a wide range of ionic liquids that have a broad spectrum of physical and chemical properties, the study on the adsorption behavior of ionic liquids with different chemical structures onto resins is important for their removal or recovery from waste streams. In the present work, the adsorption of a series of imidazolium-based ionic liquids from aqueous solutions onto five different kinds of resins was investigated with the object to understand how ILs interact with different resins as a guide to the removal of a broad base of ionic liquids from aqueous stream.

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2. EXPERIMENTAL SECTION

2.1 Materials

All ionic liquids (purity 99%) used in this work were purchased from Lanzhou Institute of Chemical Physics, Chinese Academic of Sciences (Lanzhou) and are listed in Table 1. Five types of resins were provided by Tianjin Nankai Hecheng Science & Technology Co.,Ltd, including two strong acidic cation exchange resins with sulfonic acid functionality (NKC-9 and 001×7), two weakly acidic cation exchange resins with carboxylic acid functionality (D113 and 110), and one macroporous resin without any functionality (NKA-9). The general properties of these resins are summarized in Table 2.

<Table 1 here>

<Table 2 here>

2.2 Adsorption experiments

Batch adsorption experiments were conducted in 50ml flasks containing 0.05g of resin and 20ml of ionic liquid aqueous solution with different initial concentrations. Flasks were shaken at 120 rpm in a thermostated shaker bath (DSHZ-300A, Jiangsu Peiying Experimental Apparatus Co. Ltd) at 30 ^{o}C for 5h. From the kinetics experiments, 5h was shown to be sufficient for reaching adsorption equilibrium. Solution pH was not adjusted. After equilibrium had been attained, mixtures were filtered and the concentration of the ionic liquid in the supernatant was determined using UV-VIS spectroscopy (Cary-50 Model UV, Varian Inc.) at the wavelength of 212nm for imidazolium ring[27]. All experiments were carried out in triplicate and the adsorption data shown are average values based on the triplicate experiments.

2.3 Adsorption isotherm models

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The data obtained were simulated with Langmuir (Eq. (1)) and Freundlich (Eq. (2)) models to fit the isotherms of the studied ILs. These common algorithms were used in their non-linear forms as follows[34]:

$$q_e = bq_m C_e/(1 + bC_e) \tag{1}$$

$$q_e = KC_e^{1/n} \tag{2}$$

where q_e is the equilibrium adsorption amount (mmol/g), q_m is the maximum adsorption capacity (mmol/g), C_e is the equilibrium concentration (mmol/L) of ionic liquid in solution after adsorption, b (L/mmol) is the adsorption equilibrium constant, K (L/mmol) and n are Freundlich isotherm constant related to adsorption capacity and adsorption intensity, respectively. Apparent distribution coefficients K_d (L/kg) were calculated to compare the capacity (q_e) of resins for the adsorption of ILs at a certain equilibrium concentration (C_e) with Eq. (3).

$$K_d = q_e/C_e \tag{3}$$

3. RESULTS AND DISCUSSION

3.1 Adsorption kinetics of a representative ionic liquid on the resins

As a representative and commonly used ionic liquid, [Bmim]Cl, was selected to examine the adsorption kinetics on different resins. Figure 1 shows the adsorption of [Bmim]Cl onto five resins as a function of contact time. It can be seen that equilibrium was attained in about 90 min in all cases, similar to the results reported in the other work[35]. To study the adsorption kinetics of [Bmim]Cl onto the five resins, experimental data were fit using pseudo-first-order (Eq. (4)) and pseudo-second- order models (Eq. (5)) which are given in the following forms[36]:

$$q_t = q_e(1 - e^{-k_1 t/2.303}) \tag{4}$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \tag{5}$$

where q_t and q_e are the amount of ILs adsorbed on the resins (mmol/g) at time t and equilibrium, respectively; k_1 is the adsorption rate constant of pseudo-first-order model (min^{-1}); k_2 is the adsorption rate constant of pseudo-second-order model (g.mmol^{-1}.min^{-1}).

From Figure 1 and Table 3, it can be seen that both models (Eqs. 1 and 2) fit the [Bmim]Cl adsorption data (R^2>0.98), but pseudo-first-order model was able to describe the adsorption data somewhat better than the pseudo-second-order model. The equilibrium adsorption amount q_e of these resins for [Bmim]Cl decreased in the order of NKC-9, 001×7, 110, D113 and NKA-9, implying that the functional groups attached on the resins greatly affect the recovery of the ILs with $-SO_3$ being more effective than –COOH.

<Figure 1 here>

<Table 3 here>

3.2 Adsorption isotherms of ionic liquids onto different resins

To evaluate the affinity of different resins toward ionic liquids, two common ILs, 1-Butyl-3-methylimidazolium chloride ([Bmim]Cl) and 1-Butyl-3-methylimidazolium hexafluoroborate ([Bmim][PF_6]) were selected to examine the adsorption capacity onto different resins. As shown in Figure 2(a) and Table 4, the five resins exhibited different adsorption capacity for either the hydrophobic [Bmim][PF_6] or hydrophilic [Bmim]Cl. The adsorption capacity, q_m, of the five resins for either [Bmim]Cl or [Bmim][PF_6] decreased following the same trend according to NKC-9 > 001×7 > 110 > D113 > NKA-9, inferring that the functional group attached on the resin matrix plays a key role in the adsorption of the ionic liquids onto resins. NKC-9 and 001×7 loaded with sulfonic acid groups were the most efficient for the adsorption of the ionic liquids, and exhibited high adsorption capacities above 1.6 mmol/g, which are much higher than those

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achieved in the adsorption by activated carbon (0.17 and 1.21 mmol/g for [Bmim]Cl and [Bmim][PF_6], respectively)[22, 30]. Resins 110 and D113 with carboxylic acid groups showed moderate capacities (0.2-0.7 mmol/g), while the resin NKA-9 without any functional groups displayed poor adsorption performance towards the ILs (ca. 0.06 mmol/g), although it has a BET surface area of around 200 m^2/g and a macroporous structure. Therefore, the adsorption capacities of resins for ionic liquids strongly depend on the type and concentration of the functional groups attached on the resins. Similar results were observed by Sun et al. who studied the removal of [Emim]Cl from aqueous solutions by different cationic ion-exchange resins[25]. Therefore, the adsorption capacity of an adsorbent for ionic liquids can be enhanced by addition of functional groups onto the sorbents.

<Figure 2 here>

<Table 4 here>

3.3 Adsorption of imidazolium-based ionic liquids with different anions onto different resins

To achieve desirable physical and chemical properties, different ionic liquids can be synthesized by the selection and combination of the cations and anions, leading to the production of many kinds of ionic liquids that have potential risk to the environment. Thus, it is important to investigate the adsorption behavior of ionic liquids that have different chemical structures. A series of imidazolium-based ionic liquids were selected as being representative since they are the most widely used ionic liquids.

Adsorption of ionic liquids that have a common cation 1-butyl-3-methylimidazolium, onto the five resins was studied. Experimental adsorption equilibrium data were simulated with

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Langmuir and Fruendlich models, as depicted in Figure S1. According to these fitted adsorption isotherms, apparent adsorption coefficients K_d (L/kg) were calculated at C_e =1.2 mmol/L to evaluate the adsorption capacity of the resins (Figure 3). It can be seen that for each ion-exchange resin with sulfonic or carboxylic acid groups (NKC-9, 001×7, 110 and D113), little difference could be observed in the adsorption capacity for 1-butyl-3-methylimidazolium ionic liquids with different anions, although the hydrophobicity of the studied ILs increased with increasing hydrophobicity of the IL anions that followed the sequence of $Cl^- < [PF_6]^- < [NTf_2]^-$. It seems that the anions of the ILs had little effect on the adsorption of the ILs onto the ion-exchange resins. The results are quite different with the adsorption of ionic liquids onto activated carbons where the variation of anions strongly influenced the adsorption of different ionic liquids, and the apparent adsorption coefficients K_d increased from 61 to 407 and 530 L/kg for [Bmim]Cl, [Bmim][PF_6] and [Bmim][NTf_2], respectively[22]. Therefore, it can be proposed that the ion-exchange between the cations of the resins (H^+ or Na^+) and the ionic liquids ($[Bmim]^+$) should responsible for the adsorption of ionic liquids onto the ion-exchange resins, which also resulted in a weak influence of the anion types on the adsorption capacity of the different ionic liquids onto the ion-exchange resins since these ILs have the same cation ($[Bmim]^+$).

For the macroporous NKA-9 resin without any functional groups, poor adsorption performance was shown for the studied ionic liquids (K_d < 60 L/kg), although it has a BET surface area around 200 m^2/g and a pore volume of about 1 cm^3/g. The poor adsorption capacities of NKA-9 for these ILs should be ascribed to its average pore width of about 15 nm, which is not beneficial for the adsorption of ILs, since the pores within the size range up to 8 nm were considered to play crucial role for ILs adsorption[37]. [Bmim]Cl and [Bmim][PF_6] exhibited almost

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equal adsorption uptake, but [Bmim][NTf_2] had a large increase in the adsorption capacity that should be contributed from its much higher octanol-water partition coefficient than that of [Bmim]Cl and [Bmim][PF_6][38, 39]. The phenomenon was different with the adsorption of these ILs onto the ion-exchange resins presented above. Thus, the adsorption process of ILs onto the macroporous resins and the ion-exchange resins follows different mechanisms that the former is mainly determined by polar, van der Waals and hydrogen-bonding interactions, while the latter is mainly determined by ion-exchange actions.

<Figure 3 here>

3.4 Adsorption of ILs with different alkyl chain length of imidazolium cations onto different resins

The physical and chemical properties can be changed by varying the alkyl chain length of the head group. The length of the alkyl chain of the head group should affect the adsorption capacity of the ILs onto a given resin. By fixing the head group and anion as imidazolium and Cl^-, respectively, a series of hydrophilic imidazolium-based ILs with different alkyl chain length in the head group were selected to study the effect of the alkyl chain length on the adsorption onto the resins (Figure 4(a)). It can be seen that for four ion-exchange resins with functional groups, the adsorption of the ILs on the resins was remarkably influenced by the length of the alkyl chain in the imidazolium cation, except that [Emim]Cl and [Bmim]Cl showed comparable values. The adsorption capacities increased with increasing the number of the carbon atoms in the alkyl chain of the imidazolium cation. The enhanced adsorption capacities for ionic liquids with longer alkyl chains should be attributed to the high attractive van der Waals and polar interactions between the IL and the resins[27, 40]. Moreover, the increase of the hydrophobic nature of the cation with increasing alkyl chain length could also contribute to the improved adsorption of the ILs with longer alkyl chains in the cation due to hydrophobic ionic liquid-water interactions. For the macroporous resin NKA-9, no distinct difference could be found for these ILs.

In addition, the adsorption of a series of hydrophobic ILs with PF_6^- as anion was also examined to study the effect of the alkyl chain length in the head group on the adsorption onto the resins, indicating similar characteristics to those ILs with Cl^- as anion (Figure 4(b)).

<Figure 4 here>

4. CONCLUSION

In this work, adsorption of a series of ILs with different chemical structures onto different resins was investigated. The results showed that the types of the functional groups in the resin have a strong effect on the adsorption of the ionic liquids onto the resins. The adsorption capacity of the resins for the ILs was strongly influenced by the attached functional groups in the resins, regardless of the hydrophilicity or hydrophobicity of the ILs. The resins with sulfonic acid groups, NKC-9 and 001×7, exhibited the highest adsorption capacity, followed by the resins D113 and 110 that were rich in carboxylic acid groups. The macroporous resin without any functional groups showed poor adsorption capacity for both hydrophilic and hydrophobic ionic liquids. It was found that the variation of anions of the ILs had little effect for the adsorption capacity of the resins for the ILs with the same cations but different anions. On the other hand, the length of the alkyl chain in the imidazolium cations had remarkable influence on the adsorption capacity of the ILs onto the resins, except that [Emim]Cl and [Bmim]Cl exhibited comparable values. The adsorption capacities of the resins for the ILs increased with an increase of alkyl chain length of the imidazolium cation. In summary, the ion-exchange resins were shown to be much more efficient

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than macroporous resins for the adsorption of ILs, and even exhibited higher capacities than activated carbon, demonstrating potential applications in the removal, separation and recovery of various ILs from aqueous streams.

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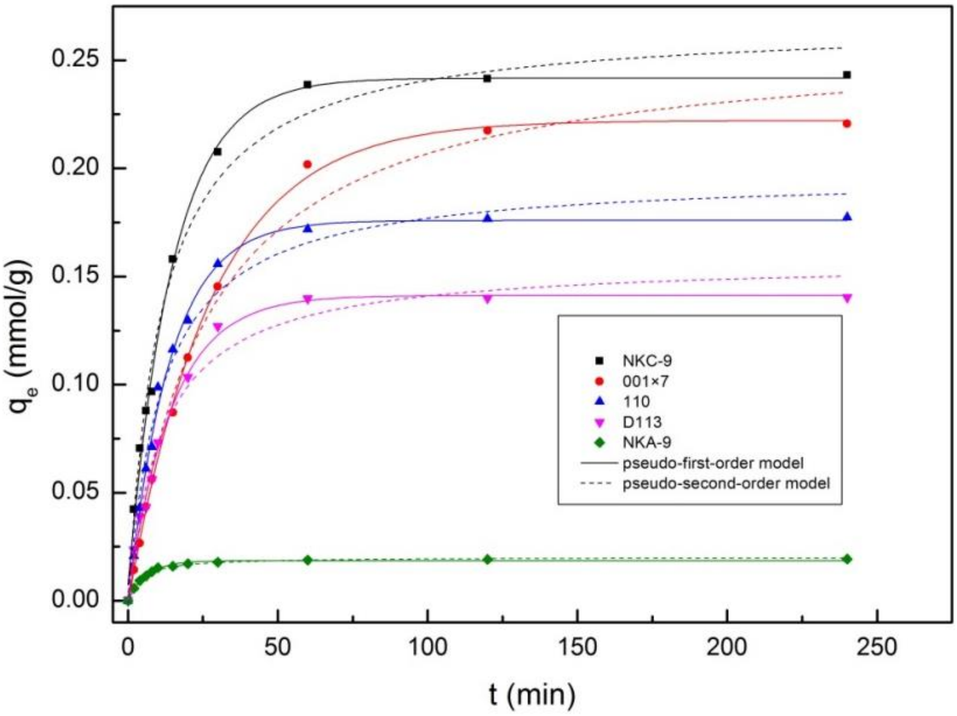

Figure 1. Adsorption kinetics of [Bmim]Cl on the different resins simulated with pseudo-first-order model and pseudo-second-order model.

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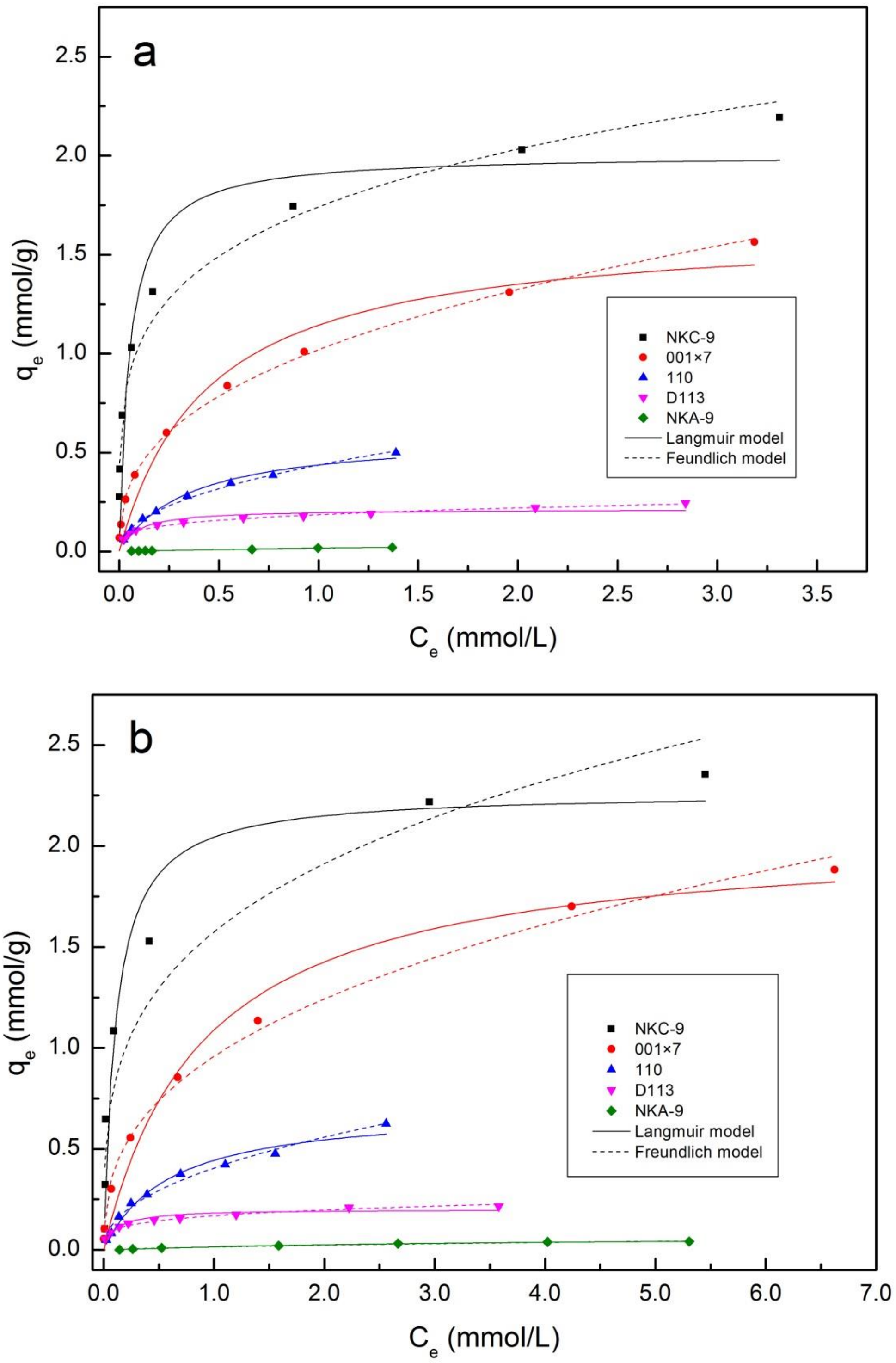

Figure 2. Adsorption isotherms of different resins for (a) [Bmim][PF_6], and (b) [Bmim]Cl with Langmuir model and Freundlich model.

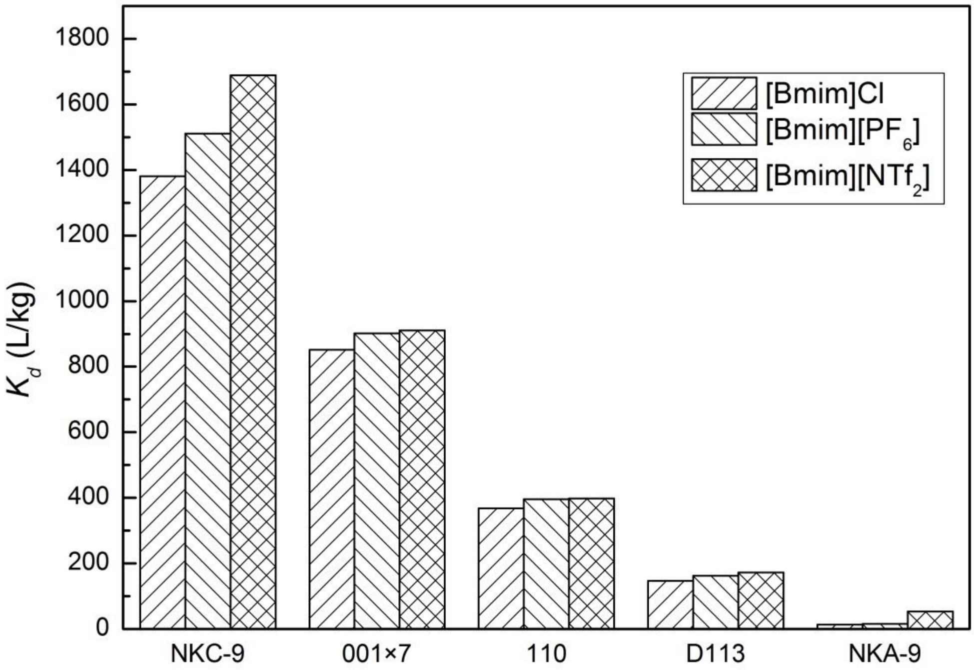

Figure 3. K_d (obtained when C_e =1.2 mmol/L) of 1-butyl-3-methylimidazolium ILs with different anions on different resins.

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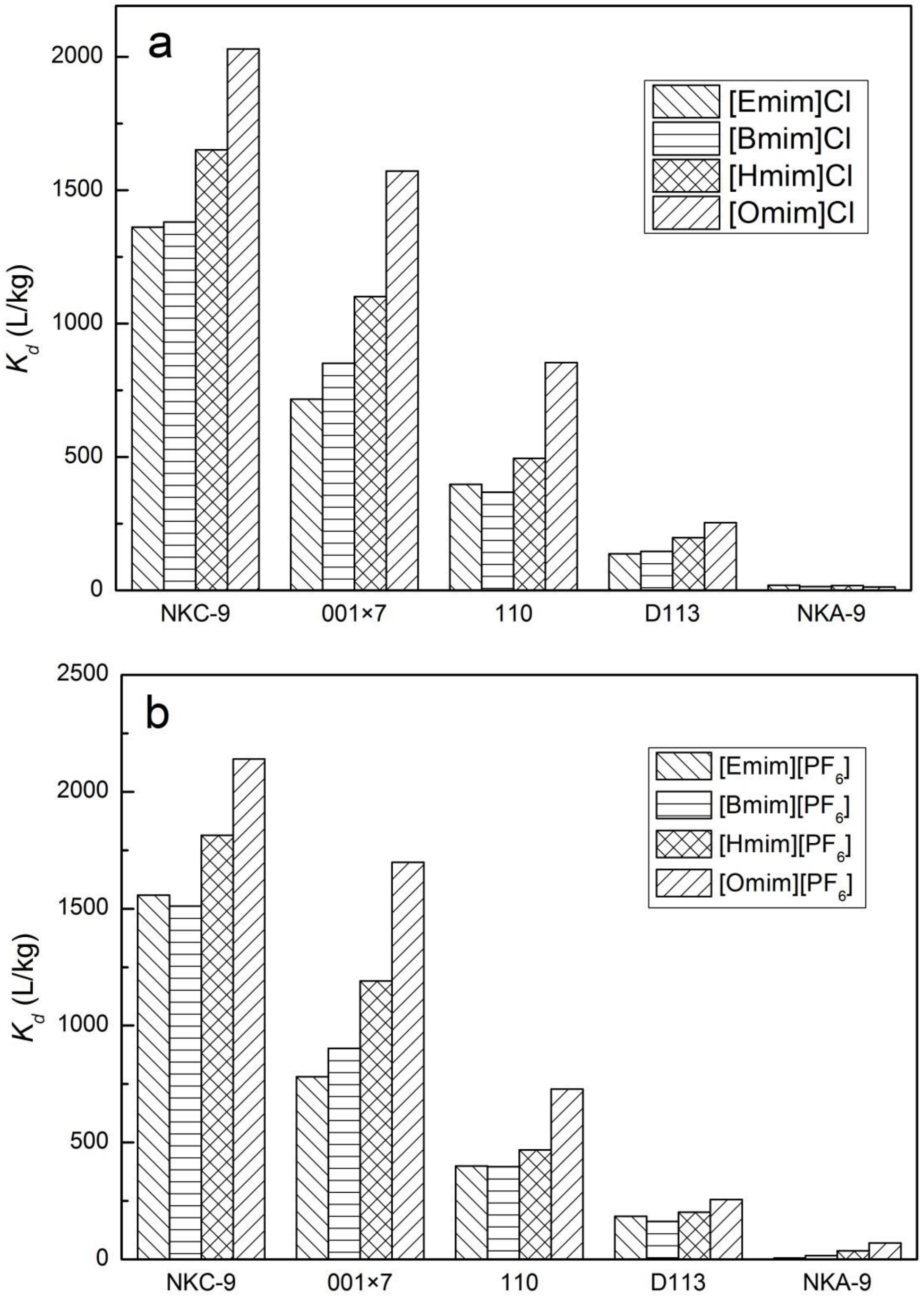

Figure 4. K_d (obtained when C_e =1.2 mmol/L) of imidazolium ionic liquids with anion (a) Cl^- and (b) $[PF_6]^-$ with different alkyl chain length on different resins.

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313 Table 1. Ionic liquids used in this work

Ionic Liquid	Acronym	Formula	Molecular Weight
1-ethyl-3-methylimidazolium chloride	[Emim]Cl	$C_6H_{11}N_2Cl$	146.6
1-butyl-3-methylimidazolium chloride	[Bmim]Cl	$C_8H_{15}N_2Cl$	174.7
1-hexyl-3-methylimidazolium chloride	[Hmim]Cl	$C_{10}H_{19}N_2Cl$	202.7
1-octyl-3-methylimidazolium chloride	[Omim]Cl	$C_{12}H_{23}N_2Cl$	230.5
1-ethyl-3-methylimidazolium hexafluoroborate	[Emim][PF_6]	$C_6H_{11}N_2PF_6$	256.1
1-butyl-3-methylimidazolium hexafluoroborate	[Bmim] [PF_6]	$C_8H_{15}N_2PF_6$	284.2
1-hexyl-3-methylimidazolium hexafluoroborate	[Hmim] [PF_6]	$C_{10}H_{19}N_2PF_6$	312.2
1-octyl-3-methylimidazolium hexafluoroborate	[Omim] [PF_6]	$C_{12}H_{23}N_2PF_6$	340.3
1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonimide)	[Emim][NTf_2]	$C_8H_{11}O_4N_3S_2F_6$	391.3
1-butyl-3-methylimidazolium bis(trifluoromethanesulfonimide)	[Bmim][NTf_2]	$C_{10}H_{15}O_4N_3S_2F_6$	419.4

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Table 2. General characteristics of four cation ion-exchange resins and one macroporous resin used in this work

Resins	Properties							
	Commercial equivalent resins	Matrix	Type	Functionality	Total exchange capacity (eq/g)	Ionic form	Surface area (m^2/g)	Appearance
NKC-9	Amberlyst 15	Styrene-DVB	macroporous	Sulfonic acid	⩾4.8(dry)	H	/	camel and opaque spheres
001×7	Amberlite IR-120	Styrene-DVB	gel	Sulfonic acid	⩾1.8	Na	/	light brown beads
D113	Lewatit CNP 80	Acrylic	macroporous	carboxylic acid	⩾4.2	H	/	beige and opaque beads
110	Amberlite IRC-84	Acrylic-DVB	gel	carboxylic acid	⩾4	Na	/	ivory-white semitransparent beads
NKA-9	/	Cross-linked polystyrene	macroporous	/	/	/	170~250	light yellow and opaque beads

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Table 3. Kinetic parameters for the pseudo-first-order and pseudo-second-order models for [Bmim]Cl adsorption onto different resins

Resins	Pseudo-first-order model $q_t = q_e(1 - e^{-k_1 t/2.303})$			Pseudo-second-order model $t/q_t = 1/k_2 q_e^2 + t/q_e$		
	$q_{e,cal}$(mmol/g)	k_1 (min^{-1})	R^2	$q_{e,cal}$(mmol/g)	k_2(gmmol^{-1}min^{-1})	R^2
NKC-9	0.241	0.155	0.996	0.268	0.089	0.988
001×7	0.222	0.083	0.999	0.261	0.038	0.986
110	0.175	0.165	0.996	0.197	0.087	0.982
D113	0.141	0.156	0.995	0.158	0.085	0.977
NKA-9	0.018	0.367	0.990	0.020	0.241	0.992

* q_e and q_t are the amount of [BMIM]Cl adsorbed on the adsorbent (mmol/g) at equilibrium and time t, respectively; k_1 is the adsorption rate constant of pseudo-first-order model (min^{-1}); k_2 is the adsorption rate constant of pseudo-second-order model (g•mmol^{-1}•min^{-1}).

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Table 4. Fitting parameters for Langmuir and Freundlich models and K_d (obtained when C_e =1.2 mmol/L) for [Bmim][PF_6] and [Bmim]Cl adsorption onto different resins

Resins	ILs	Langmuir model (Eq. 3)			Freundlich model (Eq. 4)			K_d (L/kg)
		q_m (mmol/g)	b (mmol)	R^2	K	1/n	R^2	*Ce*=1.2mmol/L
NKC-9	[Bmim][PF_6]	2.01	19.4	0.9139	1.741	0.223	0.9760	1511
	[Bmim]Cl	2.27	9.20	0.9569	1.575	0.280	0.9027	1381
001×7	[Bmim] [PF_6]	1.65	2.26	0.9655	1.020	0.378	0.9983	855
	[Bmim]Cl	2.07	1.11	0.9777	0.958	0.376	0.9942	852
110	[Bmim] [PF_6]	0.59	2.86	0.9773	0.437	0.459	0.9943	396
	[Bmim]Cl	0.71	1.70	0.9721	0.406	0.461	0.9847	368
D113	[Bmim] [PF_6]	0.21	10.9	0.8655	0.187	0.240	0.9872	162
	[Bmim]Cl	0.20	9.21	0.8920	0.169	0.227	0.9740	147
NKA-9	[Bmim] [PF_6]	0.05	0.48	0.9693	0.017	0.747	0.9786	16
	[Bmim]Cl	0.07	0.27	0.9942	0.001	0.069	0.0747	14

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