Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Information

for

Efficient and Recyclable Removal of Imidazolium Ionic Liquids from Water using Resorcinol–Formaldehyde Polymer Resin

Kun-Yi Andrew Lin and Chang-Hsuan Wu*

Department of Environmental Engineering, National Chung Hsing University,

250 Kuo-Kuang Road, Taichung, Taiwan

*Corresponding Author. Tel: +886-4-22854709, E-mail address: linky@nchu.edu.tw

(Kun-Yi Andrew Lin)

S1. Preparation of RF resin

S1.1Materials

All chemicals involved in this study were purchased from commercial suppliers and used directly without purification. Resorcinol, sodium dodecyl sulfate (SDS), and Pluronic P123 were obtained from Sigma-Aldrich (USA). Cetyltrimethylammonium bromide (CTAB) and formaldehyde were purchased from Acros Organics (USA). Sodium carbonate and sodium chloride were purchased from Showa Chemical (Japan). All ionic liquids (BMIMCl, EMIMCl, HMIMCl and BMIMBF4) were obtained from Alfa Aesar (USA). Deionized (DI) water was prepared to exhibit less than 18 MOhm-cm.

S1.2 Synthesis and characterization of RF resin

RF resin was prepared with modifications based on a reported protocol [S1] via the addition and condensation reactions as illustrated in Fig. 1 [S2]. Resorcinol (*e.g.*, 1 g) was first dissolved in 100 mL of DI water, to which 0.1 g of Na_2CO_3 was added. The solution was then heated to 40 °C and stirred until the mixture became yellowish. Subsequently, formaldehyde solution (*e.g.*, 11 mL) was dropwise added to the solution. Gelation of the resulting mixture was implemented at 85 °C for 3 days. The resulting gel was then dried at 65 °C for 1 day under reduce pressure and ground into fine powder, which was washed with acetone and oven dried to yield the final product, RF resin.

The as-synthesized RF resin was first characterized for its morphology using scanning electronic microscopy (SEM) (JEOL JSM-6700, Japan). Powder X-ray diffraction patterns (PXRD) of RF resin was measured using an X-ray diffractometer (Bruker D8 Discover, USA) with copper as an anode material (40 mA, 35 kV).

Absorption infrared (IR) spectrum of RF resin was determined using a Fourier-Transform Infrared spectrometer (Perkin Elmer Spectrum Two, USA) with KBr pellets. The molecular weight of RF resin was analyzed using a gel permeation chromatography equipped with RI detector (Schambeck SFD RI 2000, Germany).

References:

[S1] G. Zhang, C. Ni, L. Liu, G. Zhao, F. Fina, J.T.S. Irvine, Macro-mesoporous resorcinol-formaldehyde polymer resins as amorphous metal-free visible light photocatalysts, Journal of Materials Chemistry A, 3 (2015) 15413-15419.

[S2] S.A. Al-Muhtaseb, J.A. Ritter, Preparation and Properties of Resorcinol–Formaldehyde Organic and Carbon Gels, Advanced Materials, 15 (2003) 101-114.

Table S1. Thermodynamic constants of BMIMCl adsorption using RF resin

E_a (kJ mol^{-1})	A (g mg-1 m^{-1})	Temp. (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})
10.8	1.76×10^5	303	-23.34	13.2	0.12
		313	-24.44		
		323	-25.75		

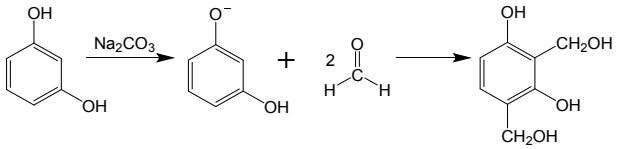
Table S2. Gibbs free energies of adsorption of EMIMCl, HMIMCl and $BMIMBF_4$ at 30 °C (303 K).

ILs	ΔG° (kJ mol^{-1})
EMIMCl	-21.10
HMIMCl	-27.75
$BMIMBF_4$	-28.25

Table S3. Comparison of RF's adsorption capacities for HMIMCl and $BMIMBF_4$ with other reported adsorbents.

Material	Ionic Liquid	Maximal adsorption Capacity	T (°C)	Reference
Macroporous Resorcinol–Formaldehyde	EMIMCl	75	30	In this study
	HMIMCl	124	30	
	$BMIMBF_4$	113	30	
Activated charcoal	HMIMCl	91	30	Palomar et al.[18]
	$BMIMBF_4$	58	30	
Oxygenated carbonaceous material	$BMIMBF_4$	80	25	Qi et al.[17]

(a) Addition reaction



(b) Condensation reaction

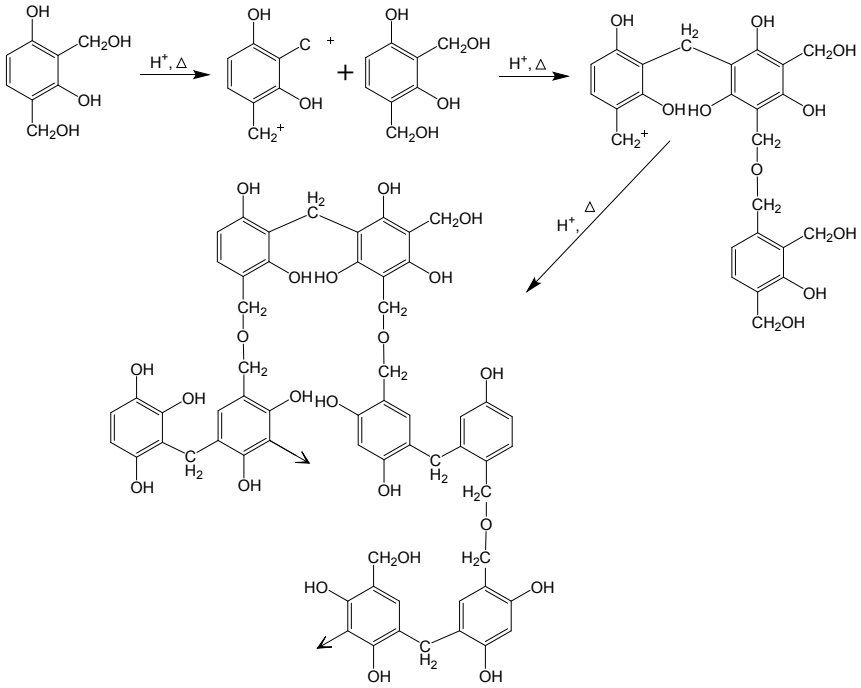


Fig. S1. Synthesis of RF resin: (a) Addition reaction and (b) Condensation reaction.

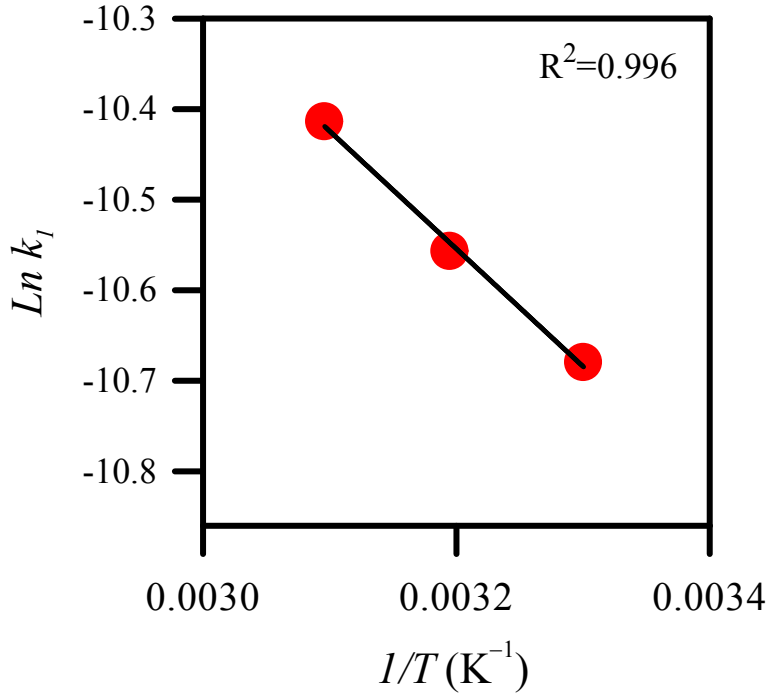


Fig. S2. A plot for determining the activation energy E_a and the temperature-independent factor k

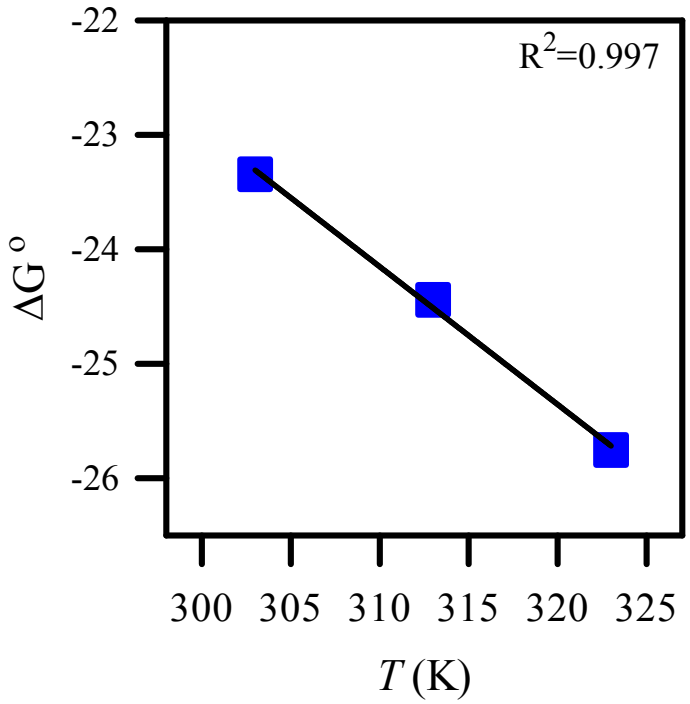


Fig. S3. A plot for determining the free energy (ΔG°), the enthalpy (ΔH°) and entropy (ΔS°) of the adsorption.