

## Removal of anionic azo dyes from aqueous solution by functional ionic liquid cross-linked polymer

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### HIGHLIGHTS

- Equilibrium, kinetic and thermodynamic of adsorption of dyes onto PDVB-IL was investigated.
- PDVB-IL has a high adsorption capacity to treat dyes solution.
- Higher adsorption capacity is due to the functional groups of PDVB-IL.
- Molecular structure of dyes influences the adsorption capacity.

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### ABSTRACT

A novel functional ionic liquid based cross-linked polymer (PDVB-IL) was synthesized from 1-aminoethyl-3-vinylimidazolium chloride and divinylbenzene for use as an adsorbent. The physicochemical properties of PDVB-IL were investigated by Fourier transform infrared spectroscopy, scanning electron microscopy and thermogravimetric analysis. The adsorptive capacity was investigated using anionic azo dyes of orange II, sunset yellow FCF, and amaranth as adsorbates. The maximum adsorption capacity could reach 925.09, 734.62, and 547.17 mg/g for orange II, sunset yellow FCF and amaranth at 25 °C, respectively, which are much better than most of the other adsorbents reported earlier. The effect of pH value was investigated in the range of 1–8. The result shows that a low pH value is found to favor the adsorption of those anionic azo dyes. The adsorption kinetics and isotherms are well fitted by a pseudo second-order model and Langmuir model, respectively. The adsorption process is found to be dominated by physisorption. The introduction of functional ionic liquid moieties into cross-linked poly(divinylbenzene) polymer constitutes a new and efficient kind of adsorbent.

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### 1. Introduction

As the largest and most versatile class of organic dyestuffs, azo dyes are widely used in textile, paper, and leather industry [1]. With the development of the industries above, a huge amount of wastewater containing azo dyes is discharged to the environment above the level that the nature can eliminate. The azo dyes and their breakdown products can cause toxic effects in the aquatic environment and are mutagenic and carcinogenic to humans [2–4]. The treatment of dye wastewater becomes more important than ever for the environment. Many technologies were applied to

treat dye wastewater, such as biological treatment [5], coagulation/flocculation [6], chemical oxidation [7], membrane filtration [8], ion-exchange [9], photocatalytic degradation [10], and adsorption [11]. Among those technologies, the most common one is the adsorption technology due to its effectiveness, efficiency, economy and no secondary pollution.

Ionic liquids (ILs) are receiving much attention owing to their unique properties, such as high thermal stability and high ionic conductivity [12]. Currently, many functionalized ILs have been used to protect water resource. Fuerhacker et al. [13] reported that the degree of removal of heavy metals (Cu, Ni and Zn) can reach 90% using quaternary ammonium and phosphonium ILs. Gharehbaghi and Shemirani [14] prepared an ionic liquid (1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imid). When it was injected into the Congo Red wastewater, most of the

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dye molecules were extracted into fine IL droplets and removed from aqueous phase. Poursaberi and Hassanisadi [15] synthesized IL@Fe<sub>3</sub>O<sub>4</sub> nanoparticles from IL-COOH and Fe<sub>3</sub>O<sub>4</sub> and found it to be an effective adsorbent of Reactive Black 5 (maximum adsorption capacity 161.29 mg/g).

The preparation of an effective adsorbent for removing anionic azo dyes from aqueous solution is expected to meet the demand of environmental protection. It is well known that the amine-functional groups on the surface of an adsorbent can greatly improve adsorption capacity [16,17]. The adsorbent with multiple benzene rings can bring  $\pi$ - $\pi$  stacking interaction between azo dye and the adsorbent, which further improves the adsorption capacity [18]. The ILs with amine groups on cross-linked polymer containing multiple benzene rings may obtain a new kind of efficient adsorbent. In this work, a cross-linked polymer is obtained by copolymerizing divinylbenzene and imidazolium ILs with an amine group. The structure of the cross-linked polymer was characterized and the physicochemical properties were investigated in detail. The adsorption capacity of functional ionic liquid cross-linked polymer was investigated in anionic azo dyes solutions.

## 2. Experimental

### 2.1. Materials

Orange II (85%), sunset yellow FCF (95%), and amaranth (98%) were obtained from Aladdin Chemical Reagent Co., Ltd. Those dye molecular structures are shown in Table 1. 1-Vinylimidazole (99%), 2,2'-azobis(2-methylpropionitrile) (99%), dimethylformamide (99%) and 2-chloroethylamine hydrochloride (99%) were purchased from Beijing Chemical Reagent Co. Divinylbenzene (DVB) (80%) was provided by Aldrich.

### 2.2. Methods

#### 2.2.1. Preparation of cross-linked polymer [19]

1-Vinylimidazole (0.1 mol) and 2-chloroethylamine hydrochloride (0.1 mol) were added into 50 ml acetonitrile. The mixture was stirred and refluxed under a nitrogen atmosphere for 48 h. The resulting solid was washed several times with anhydrous ethanol. The solid with equimolar NaOH were dissolved in water and stirred at room temperature for 24 h. After evaporating, the crude product was extracted by methanol. Then, the product was dried for 48 h under vacuum and the functional ionic liquid was obtained.

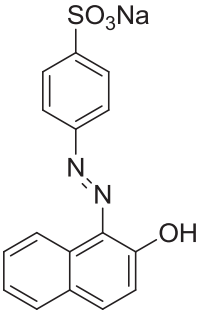
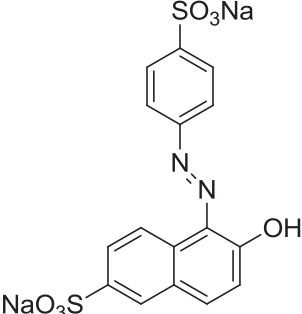
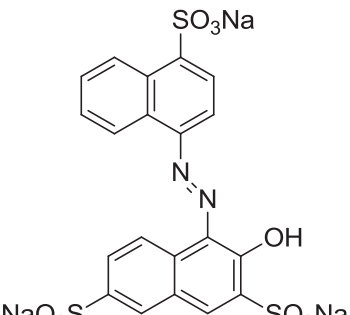
DVB (0.02 mol), 1-aminoethyl-3-vinylimidazolium chloride (0.005 mol) and an appropriate amount of 2,2'-azobis(2-methylpropionitrile) were dissolved in 50 ml dimethylformamide under nitrogen. The mixture was stirred at 80 °C for 24 h, and a yellow solid was collected by filtration and washed with acetone. The adsorbent of poly(divinylbenzene-co-1-aminoethyl-3-vinylimidazolium chloride) was obtained.

The synthetic process of PDVB-IL is shown in Fig. 1.

#### 2.2.2. Characterization of the adsorbent

The Fourier transform infrared (FT-IR) spectra of PDVB-IL, PDVB-IL-Orange II (after adsorption of orange II on PDVB-IL) and orange II were obtained on VERTEX-70 FT-IR spectrometer using KBr pellet in the range of 4000–400 cm<sup>-1</sup>. The particle size and morphology of PDVB-IL were characterized using a scanning electron microscope (SEM, JSM-7600F, EOL, Ltd., Japan). The N<sub>2</sub> adsorption-desorption isotherm for sample was measured at 77 k with a Quadrasorb Station 2 Analyzer (Quantachrome, USA). Thermogravimetric analysis (TGA) was carried out using a Rheometric Scientific TGA1500 (Piscataway, NJ) to investigate the thermal properties of samples. Studies were conducted under inert atmosphere of nitrogen using

**Table 1**  
Characteristics and structures of anionic azo dyes.

Generic name	M.W.	$\lambda_{\max}$ (nm)	Molecular structure
Orange II	350.32484		
Sunset yellow FCF	452.38482		
Amaranth	604.47521		

8–10 mg samples at a heating rate of 10 °C/min in the range of ambient temperature to 800 °C.

#### 2.2.3. Batch adsorption procedure

Batch adsorption was carried out in order to evaluate the adsorption capacity. The three dye solutions were prepared by dilution of the stock standard solution (dye solution 200 mg/L). All batch adsorption experiments were carried out as follows: 20 mL dye solutions and 2 mg PDVB-IL were poured into 100 mL conical beaker. The conical beaker was shaken by the oscillator (SHZ-82, Changzhou Shaipu Experimental Instrument Factory, China) at a speed of 150 rpm. After centrifugation, the solution absorbance was measured using UV-vis-NIR spectroscopy (Hitachi U-4100, Japan) with the  $\lambda_{\max}$  at 484, 482 and 520 nm for orange II, sunset yellow FCF and amaranth, respectively. The amount of adsorbed dye on PDVB-IL ( $q$ , mg/g) was calculated according to the following equation:

$$q = \frac{C_0 - C_f}{m} V \quad (1)$$

where  $C_0$  is the initial concentration of dyes in solution (mg/L),  $C_f$  is the dyes concentration at equilibrium (mg/L),  $m$  is the mass of adsorbent (g), and  $V$  is the volume of solution (L).

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