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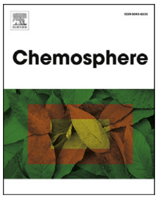

# The oxidative degradation of polystyrene resins on the removal of Cr(VI) from wastewater by anion exchange

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## HIGHLIGHTS

- Oxidation of Cr(VI) significantly influenced Cr(VI) removal and resin properties.
- The cleavage of the C—N bonds led to a decrease of the resin sorption capacity.
- The cleavage of the C—C bonds resulted in the degradation of the resin matrix.
- Cr(III) was mainly eluted as amphoteric hydroxide in the regeneration process.

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## ABSTRACT

Cr(VI) is a powerful oxidant and is capable of oxidizing most of the organic materials. Therefore, it is possible for Cr(VI) to oxidize the polymeric resins and change the sorption properties of the resins on the removal of Cr(VI) from wastewater by anion exchange. In this study, three polystyrene resins (D201, D202, and D301) with different functional groups ($-N^+(CH_3)_3$, $-N^+(CH_3)_2(C_2H_4OH)$, and $-N(CH_3)_2$) were assessed on oxidation stability for Cr(VI) removal from wastewater in fixed-bed column experiments. After a 10-cycle operation, due to the oxidation of the resin, the sorption capacity of D201, D202, and D301 resins decreased by 23.5, 29.3, and 17.3%, when approximately 20–34%, 31–50%, and 18–30% of Cr(VI) was reduced to Cr(III) during each cycle respectively. The results of the Fourier transform infrared spectroscopy (FT-IR) showed that both the cleavage of C—N and the formation of C═O bonds occurred on the polystyrene resins during the Cr(VI) removal process. The resin simulation experiments further validated the oxidation of C—C and C—N bonds connected with phenethyl groups. Based upon the results from column operations and the resin simulated experiments, the oxidation mechanism of the polystyrene resin was proposed.

## 1. Introduction

Cr(VI) is a heavy metal that requires more attention to deal with it in wastewater. The effluents from many industries, such as mining operations, metal-plating facilities and power generation facilities, contain Cr(VI) in concentrations ranging from tens to thousands of mg/L (Owlad et al., 2009). However, Cr(VI) is known to be toxic to both plants and animals as a strong oxidizing agent and potential carcinogen. Because of the high toxicity in the environment, the discharge of Cr(VI) to surface water is regulated to below 0.05 mg/L by the U.S. EPA (Park et al., 2004). Consequently, Cr(VI) removal technology has been of great interest in recent years (Augustynowicz et al., 2010; Pan et al., 2014a).

In the past decades, ion exchange has attracted increasing attention for reducing Cr(VI) concentrations to near-zero levels due to its simple operation, small sludge production, and recovery and reuse of Cr(VI) (Bajpai et al., 2012; Yang et al., 2014). Although sorption of Cr(VI) by ion exchange resin is mainly a result of ion exchange, it is also influenced by the nature of the resin functional groups. Most of the resins, which exhibited high selectivity for Cr(VI) and satisfactory Cr(VI) removal efficiency, had type I ($-N^+(CH_3)_3$) quaternary ammonium functional groups in their structures (Mustafa et al., 2010; Yang et al., 2014). For example, Lewatit MP500 exhibited a good selectivity for $CrO_4^{2-}$ anions.

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However, this was due to the reason that the selectivity sequence of common anions in wastewater was $CrO_4^{2-} > SO_4^{2-} > Cl^- > OH^-$ (Untea et al., 2002). Furthermore, Dowex 1 × 8 exhibited a large exchange capacity (0.54 mmol/g resin) and a rapid ion-exchange rate for the removal of Cr(VI) from the aqueous solution (Edebali and Pehlivan, 2010). Strong-base anion exchangers with type II ($-N^+(CH_3)_2(C_2H_4OH)$) functional groups, which usually have a greater capacity than type I, were also researched for the removal of Cr(VI) (Gode and Pehlivan, 2005). Compared to the strong-base anion exchange resins, weak-base resins with tertiary amine groups ($-N(CH_3)_2$) exhibited large sorption capacity and high regeneration efficiency (Galan et al., 2005; Shi et al., 2009). A number of studies claimed that the weak-base anion exchangers (such as Lewatit MP62, Lewatit MP64, Lewatit M610 and Amberlite IRA96) with macroporous structures, exhibited good Cr(VI) retention capacities (i.e., 0.40–0.54 mmol/g) at the optimal sorption conditions (Gode and Pehlivan, 2005; Pehlivan and Cetin, 2009; Edebali and Pehlivan, 2010).

It is well known that Cr(VI) is a powerful oxidant and is capable of oxidizing almost all the organic materials (Brose and James, 2010); therefore, it is often used in COD measurement (Domini et al., 2006), in which Cr(VI) is reduced into Cr(III) (Lv et al., 2011). Our previous investigation found that during the Cr(VI) sorption process, the polymeric resins were oxidized due to the strong oxidizing capability of Cr(VI), which changed the sorption properties of the resins (Xiao et al., 2016). The key parameters influencing the oxidation were also studied. Because of protons and electrons involved, the resin oxidization was highly dependent on solution pH and initial concentration of Cr(VI). The reduction rate of Cr(VI) increased sharply with increasing initial concentration of Cr(VI) and decreasing solution pH (Xiao et al., 2016). Although a general consensus seems to exist on the oxidation of polymer resins, little is known about the detailed oxidation mechanism of the polystyrene resins which have been widely used for the treatment of Cr(VI)-containing wastewater.

Commercially, anion exchange resins are classified as strong-base resins which include type I ($-N^+(CH_3)_3$) and type II ($-N^+(CH_3)_2(C_2H_4OH)$) quaternary ammonium functional groups and weak-base resins which typically include tertiary amine groups ($-N(CH_3)_2$). In the present study, the difference in the oxidation stability of the polystyrene resins (D201, D202, and D301) with varied functional groups ($-N^+(CH_3)_3$, $-N^+(CH_3)_2(C_2H_4OH)$, and $-N(CH_3)_2$) towards the removal of Cr(VI) was examined using column operations. Then, experiments were also conducted to explore the oxidation mechanism of the studied resins.

## 2. Materials and methods

### 2.1. Materials and chemicals

For comparison, the commercial resins in the chloride form, D201, D202, and D301, were provided by Zhejiang Science Co. Ltd. The relevant physico-chemical properties of these resins supplied by the manufacturer are listed in Table S1. The purity of ar-ethenyl-N,N,N-trimethyl-chloride (CAS:26616-35-3, ETC), benzyl-(2-hydroxyethyl) dimethylammonium chloride (CAS:7221-40-1, BDC), and N-(4-vinylbenzyl)-N,N-dimethylamine (CAS:2245-52-5, VND) was approximately 95–97%.

### 2.2. Columns experiments

The sorption and regeneration experiments were performed in a transparent glass column (2.8 cm i.d. × 32 cm length, with an effective column height of 30 cm) at around 25 °C. The synthetic solution (initial Cr(VI) concentration of 500 mg/L and pH 2.0) was fed (at a rate of 10.4 mL/min) from the feed tank into the bottom of the glass column using a peristaltic pump, percolated upward through the resins, and then finally discharged into the corresponding effluent tank. When the concentration of Cr(VI) was greater than 0.5 mg/L, the regeneration of the resin was required. The acid-alkali method was used to regenerate the exhausted resin (Xiao et al., 2016). The eluate of the regeneration process was collected in a spent brine vessel.

This test was conducted using up to 10 sorption–regeneration cycles. At the end of every cycle, samples were individually taken from their corresponding tanks to measure water quality. The sorption capacity ($q_e$) of each resin was calculated by the following mass-balance equation:

$$q_e = \frac{(C_{in} - C_{Cr}) \times V_{eff}}{m} \tag{1}$$

where $C_{in}$ is the initial $C_{Cr(VI)}$, mg/L; $C_{Cr}$ is the concentration of total Cr in the effluent tanks, mg/L; $V_{eff}$ is the volume of the produced Cr(VI) solution, L; $m$ is the mass of resin used, g.

### 2.3. Resin simulation experiments

The resin simulation experiments were performed in flasks. The following set of factors were selected as the standard conditions: 2 mmol/L substitute for the polystyrene resins (ETC, BDC, or VND), 500 mg/L initial Cr(VI) concentration, 1000 mL working volume, and pH 2 at room temperature. The flasks were purged with $N_2$ gas to remove $O_2$ from the system. Sufficient solution/substitute contact time was allowed until the Cr(VI) concentration reached a constant value. Samples were successively collected from the flasks at regular intervals of 8 h.

### 2.4. Chemical analysis

The concentration of Cr(VI) was analyzed by the 1,5-diphenyl carbazide method. The total Cr concentration was measured by the addition of excess potassium permanganate to oxidize the Cr(III) to Cr(VI) at boiling conditions for approximately 20 min prior to the performing the 1,5-diphenyl carbazide method. The concentration of Cr(III) was calculated as the difference between the total chromium and Cr(VI) concentrations (Pan et al., 2014b).

The X-ray photoelectron spectroscopy (XPS) spectrum of the resin was recorded by using an X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo-Fisher) equipped with Mg Ka X-ray source (power of 300 W). The FT–IR spectrum of the resin was obtained using an Agilent 5500a instrument, with KBr pastille (sample/KBr ratio of 1:100). GC–MS was performed using a 450 GC–MS apparatus (Bruker, USA), fitted with DB-5 capillary column (30 m, 0.25 mm i.d., 2-lm film; Varian).

## 3. Results and discussion

### 3.1. Formation of Cr(III)

Cr(VI) is a powerful oxidant, thus it is easily reduced to Cr(III) (de Souza et al., 2016), as shown in the following equation (Gagrai et al., 2013):

$$Cr(VI) + H^+ + 3e^- \rightarrow Cr(III) + H_2O \tag{2}$$

For the reduction of Cr(VI) to Cr(III), electrons supplied by the resins are consumed, which results in the oxidation of the organic compounds of the resins. As shown in Eq. (2), the quantity of Cr(III) generated is in proportion to the depletion of electrons, which can