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Comparative adsorption of glyphosate from aqueous solution by 2-aminopyridine modified polystyrene resin, D301 resin and 330 resin: Influencing factors, salinity resistance and mechanism

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ABSTRACT

Comparative adsorption of glyphosate from aqueous solution by 2-aminopyridine modified polystyrene resin (denoted GQ-08 resin), D301 resin and 330 resin was investigated with respect to influencing factors, salinity resistance and mechanism. Results showed the maximum adsorption capacity of glyphosate onto the three resins was observed at pH of 2.51, and glyphosate was adsorbed in the form of $HO-PO_2^- -CH_2-NH_2^+ -CH_2-COOH$ and $HO-PO_2^- -CH_2-NH_2^+ -CH_2-COO^-$. The adsorption capacity of glyphosate onto the three resins followed the order 330 resin > D301 resin > GQ-08 resin, consistent with their total exchange capability order. GQ-08 resin exhibited excellent salinity resistance. Salinity resistance of GQ-08 resin resulted from the hydrogen bonding for the adsorption of glyphosate, while 330 resin and D301 resin exhibited the single adsorption mechanism of anion exchange.

1. Introduction

Glyphosate (N-(phosphonomethyl) glycine) is a nonselective, highly effective, post-emergence herbicide used globally in agriculture [1,2]. As the most used herbicide, glyphosate is been used widely for the control of annual and perennial weeds, particularly in sugarcane plantations [3]. Due to the vast demand for glyphosate, it is now representing 60% of the global herbicide sales [4]. There are more than 49 producers with the production of 72,000 tons per year in china, and its impact on the environment is becoming more and more outstanding [5].

In glyphosate industrial production, glyphosate can be synthesized by glycine-dimethyl phosphate technique [6,7]. The technique produces a large amount of mother liquor with about 1.5% glyphosate, 15% NaCl and other organic by-products [7]. It is obvious that the direct discharge of the mother liquor can cause severe impacts on the water environment. How to effectively and economically recover glyphosate from the mother liquor in the factory is being an interesting subject. The evaporation concentration is a traditional method to treat glyphosate mother liquor in China [8]. However, large energy has to be consumed in the method. Another traditional method is that glyphosate mother liquor is diluted by freshwater and then is subjected to other physicochemical treatments [6]. The obvious drawback of the method is that the huge amount of freshwater is used up and no glyphosate is recovered. Several other methods, such as chemical oxidation [9], microbial degradation [10], photocatalytic degradation [11] and membrane separation [6], have been used to deal with this mother liquor. Some of these procedures have some drawbacks of inapplicability to large scale units, expensive investment, chemical intensiveness and secondary pollutions.

Polymeric adsorbents have some good characteristics of stable framework, good mechanical strength, great adsorption capacity and feasible regeneration for repeated use [12–14]. The use of polymeric adsorbents to recover organic pollutants from aqueous solution has been more and more attractive [15,16]. Glyphosate exhibits high solubility in aqueous solution [17]. Glyphosate can react with both acid and alkali because of three functional groups (NH, COOH, and H_2PO_3). So, it is difficult for glyphosate to be adsorbed onto polymeric adsorbents especially under the condition of high concentration of co-existing salinity. Up to now, the successful adsorption of glyphosate onto polymeric adsorbent under the condition of high concentration of co-existing salinity has not been reported publicly. The aim of this work is to investigate the influencing factors, salinity resistance and adsorption mechanism

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of glyphosate onto GQ-08 resin, D301 resin and 330 resin.

2. Experimental

2.1. Material and chemicals

D301 resin and 330 resin were purchased from Zhejiang Zhengguang Industrial Co. Ltd. (Zhejiang province, China). D301 resin is a macroporous, weak base anion exchange resin with polystyrene matrix, amino functional groups, the total exchange capability 4.8 mmol/g 330 resin is a gel, weak base anion exchange resin with epoxy matrix, amino functional groups, the total exchange capability 9.0 mmol/g. Before use, D301 resin and 330 resin were rinsed with 1 mol/L HCl, ultrapure water, 1 mol/L NaOH and ultrapure water by turns, and then were stored in ultrapure water respectively. Macroporous crosslinked chloromethylated polystyrene beads were purchased from Nankai Group the Chemical Plant of NanKai University (Tianjin, China), its cross-linking degree, 6%; chlorine content, 17.61%. All of the reagents were of analytical grade. Ultrapure water was used to prepare all solutions throughout the experiments. The standard glyphosate was purchased from Sigma–Aldrich (Steinheim, Germany).

2.2. Synthesis of GQ-08 resin

As described in Scheme 1 and 20 g chloromethylated polystyrene beads were swollen in 300 mL of 1,4- dioxane at 298 K for 12 h. 72.5 g 2- aminopyridine was added into the flask quickly. Under the condition of nitrogen, the mixture was further reacted at 80 °C for 12 h. At the end of the reaction, the mixture was filtered. The polymer beads were rinsed with 1,4- dioxane and ethanol by turns. The polymer beads were immersed in 2% NaOH solution to remove the acid generated by the reaction, then rinsed with ultrapure water until the water flowing from the rinsed resins was neutral, and extracted with ethanol in a Soxhlet apparatus for 12 h and dried at 313 K in vacuum (<10 mm Hg). The dried sample of the polymer beads modified with 2- aminopyridine was named as GQ-08 resin.

2.3. Characterization of the resins

FT-IR spectra of all samples, dispersed in KBr, were obtained on the Nexus 870 Fourier transform infrared spectrometer. Elemental analysis of N was carried out using the Elementar Vario MICRO. Elemental analysis of Cl was determined by Volhard method [18]. Total exchange capability was measured with acid-base neutralization titration method [15].

2.4. Adsorption assay

Equilibration experiments of glyphosate onto the three resins were performed at a given temperature. About 0.1 g resin and 50 mL of glyphosate solution were added into a series of 100 mL conical flasks. The initial concentrations of glyphosate solution ranged from 0.6 mg/mL to 1.5 mg/mL. The flasks were shaken in a thermostated rotary shaker with the speed of 150 rpm to equilibrate. The supernatants were filtered using a 0.45 μm disposable membrane filter to determine the concentration of glyphosate. HCl or NaOH was used to adjust initial pH of the solution of glyphosate.

The amount of glyphosate adsorbed by the three resins was calculated by the following mass balance equation:

$$q_t = \frac{V(C_0 - C_e)}{m} \quad (1)$$

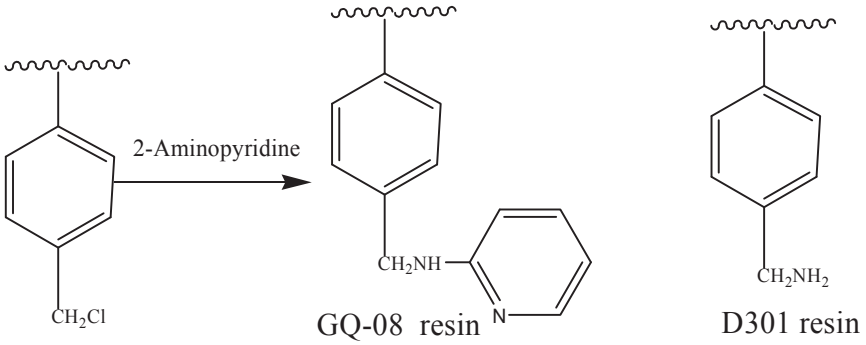
where q_t (mg/g) was the adsorption amount of glyphosate, V (mL) was the volume of the solution of glyphosate, m (g) was the mass of dry resin, C_0 (mg/mL)and C_e (mg/mL) were the concentration of glyphosate at initial and at equilibrium, respectively.

3. Results and discussion

3.1. Characterization of the resins

Fig. 1 shows the FT-IR spectra of chloromethylated polystyrene and GQ-08 resin. IR absorption bands at 1260 and 673 cm^{-1} correspond to the characteristic adsorption peaks of CH_2Cl group of chloromethylated polystyrene. On the contrary, the two strong characteristic peaks attributed to the CH_2Cl group at 1260 and 673 cm^{-1} in GQ-08 almost disappear after the nucleophile substitution reaction. A characteristic vibration band appears with frequency at 1580 cm^{-1}, which is representative of the pyridine group. Vibration peaks with frequencies at 769 cm^{-1} and 1650 cm^{-1} are presented, which are concerned with the characteristic bending vibration peaks of the N–H.

As shown in Table 1, the content of Cl of chloromethylated polystyrene is up to 17.61% determined by the Volhard method, while the content of Cl of GQ-08 resin decreases to 1.43%. The content of N of chloromethylated polystyrene is 0%, while the content of N of GQ-08 resin is up to 9.74% after the nucleophile



Scheme 1. Structure of GQ-08 resin, D301 resin and 330 resin.