

# Adsorption of glyphosate from aqueous solution onto surfactant-modified resin

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**Abstract.** Nano-iron and copper oxides loaded weakly basic resin D301 was investigated for the removal of glyphosate from aqueous solution. The characteristics of the resin before and after surfactant-modification were examined using scanning electron microscopy and Fourier transform infrared spectroscopy. The effects of pH, contact time, temperature and coexisting humic acid and fulvic acid were studied by batch adsorption. Adsorption of glyphosate was found strongly affected by the pH, with pH 3 providing maximum adsorption of glyphosate from aqueous solutions. The pseudo-first-order rate and pseudo-second-order rate models were applied to the experimental data. Glyphosate adsorption clearly followed the pseudo-second-order model. Moreover, fulvic acid had obvious effect on glyphosate adsorption.

## Introduction

A macroporous anion exchanger resins such as D301 and D201 have been regarded as excellent adsorbents to remove numerous organic pollutants due to large adsorption capacity[1,2]. However, the adsorption capacity of D301 may decrease greatly with the coexisting of chloride ion and other anions. Nano-metal oxides have high specific surface area, short intraparticle diffusion distance and good surface chemistry property[3]. Therefore, the combination of nano-metal oxides and resin probably has excellent selectivity on the treatment of pollutants. Glyphosate (N-(phosphonomethyl) glycine, Gly) is a highly effective post-emergence and non-selective herbicide that has been widely applied in agriculture[4,5]. Glyphosate gets into the water and soil, and it will induce disruption of brain intelligence, reproductive and nervous system[6]. Nano-iron and copper oxides loading D301 composite resin(NICO-D301) was prepared and used for removal a Gly from water.

## Materials and methods

**Chemicals and reagents.** D301 resin was from Nankai Resin Co. Ltd. (Tianjin, China). Gly was from QiaoChang Chemical Co. Ltd.(Binzhou, China). All chemicals used were of analytical reagent grade and obtained from Shanghai Chemical Reagent Station (Shanghai, China).

**Preparation of NICO-D301.**The NICO-D301 were synthesized as followings: a certain amount of weakly basic anion exchanger resins were added into a  $\text{CuCl}_2 + \text{FeCl}_3 + \text{NaCl} + \text{HCl}$  mixed solution, followed by continuous agitation for 24 h with a thermostat and shaken at 120 rpm at 298 K. Then the resins were filtered out and then placed in the 2 mol/L of NaOH solution quickly. The obtained composites were washed with ethanol until no floc appeared, washed with distilled water until the pH was neutral and then dried in a vacuum oven at 303 K for 24 h. The as-prepared sample was denoted as DHIO-WR.

**Batch adsorption.** Batch adsorption studies were performed by mixing 100 mg of NICO-D301 with 100 mL of Gly solution at concentration (400mg/L) in a 250 mL glass flask at different temperature. After pre-defined contact time, the aqueous sample was filtered and was determined with HPLC. The effect of solution pH on Gly adsorption was investigated by adding sulfuric acid or sodium hydroxide into Gly solutions (400 mg/L) to adjust different pH values at 303 K. After 24 h, the aqueous samples were filtrated, and the concentrations of Gly were determined with HPLC. The effect of humic acid

and fulvic acid on Gly adsorption was carried out by shaking 100 mg of NICO-D301 in 100 mL of solutions with different concentrations of humic acid and fulvic acid (0, 50, 100, 150, 200, 300 and 400 mg/L) and an initial Gly concentration of 400 mg/L at 303 K.

**Glyphosate analysis.** The Gly concentrations were determined by high-performance liquid chromatography (HPLC, Waters 2695, Waters Corporation, USA) separation was performed using a strong anion exchange (SAX) column (250 mm×4.6 mm internal diameter, particle size 5.5 mm; Elite, Dalian, China). The mobile phase was methanol-water (15/85, v/v) containing 0.5%  $\text{KH}_2\text{PO}_4$  as a pH regulator. The mobile-phase flow rate was  $0.8 \text{ cm}^3/\text{min}$ , and the detector wavelength was 195 nm. Under these conditions, the retention time for Gly was 7.0 minutes.

## Results and discussion

**Characterization of NICO-D301.** The FT-IR spectra of D301, NICO-D301 and NICO-D301+Gly are shown in Fig. 1. The FT-IR spectrum of D301 showed a broad absorption band around  $3500 \text{ cm}^{-1}$ , which may be attributed to the O-H group. The bands at  $1640$  and  $1460 \text{ cm}^{-1}$  were from aromatic C-C stretching in the phenyl ring. The intense band at  $1376 \text{ cm}^{-1}$  corresponded to the characteristic C-N stretching vibration of amine groups in the resin. There were also fewer bands in the fingerprint region of NICO-D301 compared to that of D301. The bands at  $425$  and  $530 \text{ cm}^{-1}$  can be assigned to the stretching vibration of Fe-O and Cu-O in NICO-D301. These observations clearly indicated that iron and copper oxides loaded on the surface of D301. The intense band at  $1190 \text{ cm}^{-1}$  corresponded to the characteristic P=O stretching vibration of Gly.

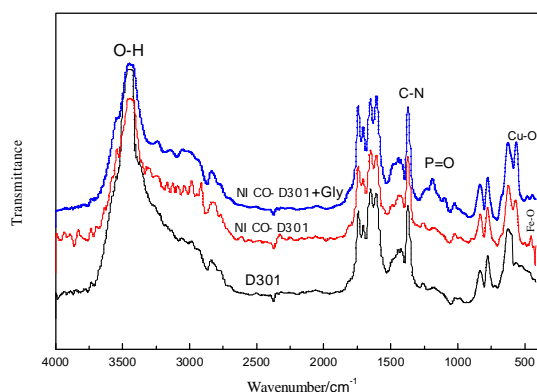


Fig. 1. FTIR spectrum of D301, NICO-D301 and NICO-D301+Gly.

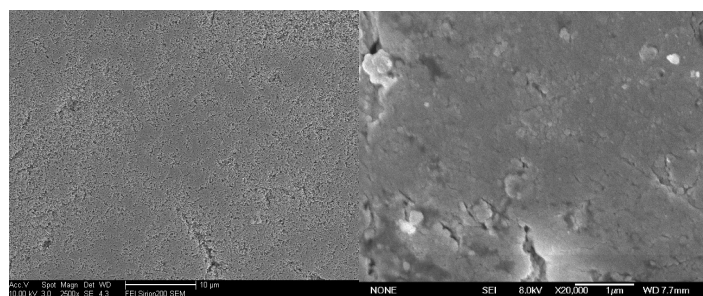


Fig. 2. Morphology of resin a=D301 and b=NICO-D301.

SEM micrographs of the D301 and NICO-D301 resin are shown in Fig. 2. The nano-iron and copper oxides were evenly distributed on the D301 resin (Fig. 2b) and the surface morphology of NICO-D301 resin was different from that of the D301 resin. A rough surface and abundant pores would provide convenient diffusion channels for ions onto the NICO-D301 resins when they were used for adsorption in aqueous solution.

**Effect of pH.** The pH is one of the most important factors affecting the adsorption process. The adsorption of Gly onto NICO-D301 as a function of solution pH is shown in Fig. 3. Results showed that the adsorption capacity of NICO-D301 for Gly decreased with increasing solution pH from 3 to 12. This observation is explained as follows. Gly is a weak organic acid, and contains a phosphonate, a carboxylate and an amine group. So its ionization is strongly dependent on solution pH [9] and its  $\text{pK}_{a1}$ ,  $\text{pK}_{a2}$  and  $\text{pK}_{a3}$  was 2.20, 5.46 and 10.14, respectively. At solution pH below 5.46, the adsorption of Gly onto the positively charged surface of NICO-D301 is unlikely to be driven by the electrostatic attraction. Meanwhile, the adsorption of Gly mainly relied on the innersphere complexation with the iron oxide and copper oxide nanoparticles. Therefore, the electrostatic attraction together with the coordinate bond are responsible for the NICO-D301 adsorption to Gly.

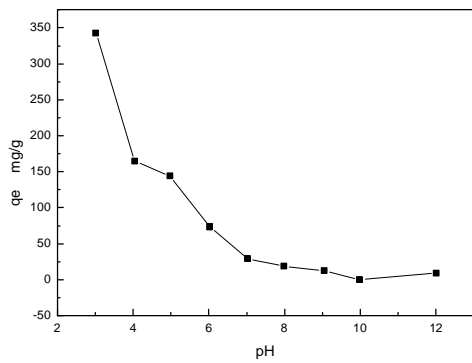


Fig. 3 Effect of solution pH on the adsorption of Gly by NICO-D301 at 303K and initial Gly 400 mg/L.

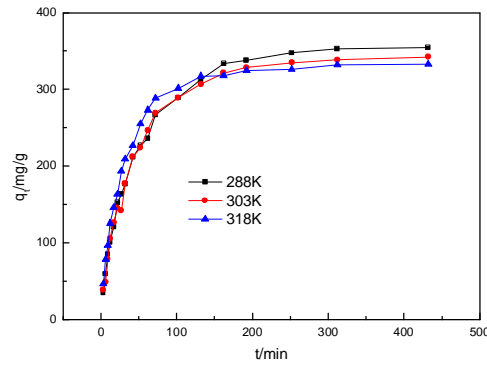


Fig. 4 Effect of contact time on the adsorption of Gly by NICO-D301 at 288, 303 and 318 K and initial Gly 400 mg/L.

**Effect of contact time.** The effects of contact time on the Gly adsorption onto NICO-D301 are shown in Fig. 4. Results showed that the adsorption capacity increased rapidly at the beginning and thereafter it proceeded at a platform. It was observed that the removal efficiency of Gly in the first 3 h reached to 95.2%, 95.9% and 97.6% at 288 K, 303K and 318K, respectively. The adsorption of Gly was reached its equilibrium in 7 h for NICO-D301.

Table 1 Parameters for glyphosate adsorption by DR according to different kinetic models.

Kinetic parameters		288K	303K	318K
Pseudo First order	$k_1/(\text{min}^{-1})$	0.0094	0.0091	0.0101
	$R^2$	0.9125	0.8929	0.9300
Pseudo Second order	$q_e(\text{mg}\cdot\text{g}^{-1})$	384.62	370.37	357.14
	$k_2/(\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1})$	0.000076	0.000083	0.000134
	$R^2$	0.9990	0.9983	0.9992

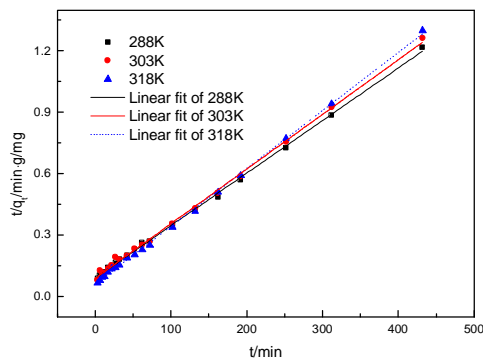


Fig. 5 Experiment data for pseudo-second-order model fit on Gly adsorption by NICO-D301 at 288, 303 and 318 K and initial Gly 400 mg·L<sup>-1</sup>.

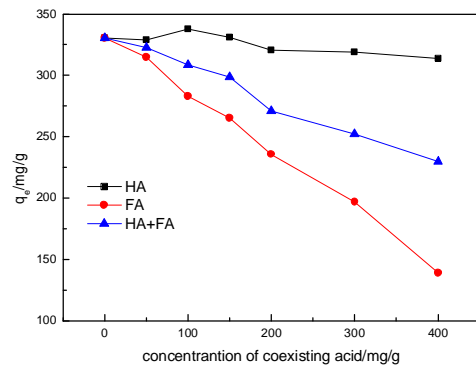


Fig. 6 Effect of competing acid on the adsorption of Gly by NICO-D301 at 303K and initial Gly 400 mg·L<sup>-1</sup>.

To investigate the mechanism of adsorption process, the pseudo-first-order rate adsorption model (Eq. (1)) and pseudo-second-order rate adsorption model (Eq. (2)) are employed to interpret the kinetics results[7,8].

$$\lg(q_e - q_t) = \lg q_e - k_1 t \tag{1}$$

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

Where,  $q_e$  (mg·g<sup>-1</sup>) and  $q_t$  (mg·g<sup>-1</sup>) are amount of the adsorbate adsorbed on the adsorbent at equilibrium and at time t (h), respectively. The  $k_1$  and  $k_2$  are the pseudo-first-order rate constant and the pseudo-second order adsorption rate constant, respectively. The parameters of two kinetic models and correlation coefficients  $R^2$  of NICO-D301 under different conditions were calculated from these

plots, and are given in Table 1. The values of adsorption capacity (Fig. 5) calculated from the pseudo-second-order kinetic equation are more close to the values observed experimentally. The  $R^2$  value obtained from pseudo-second-order kinetic model are larger than 0.99. From these results, the Gly adsorption onto NICO-D301 could be described by the pseudo-second-order kinetic model.

**Effect of coexisting humic acid and fulvic acid.** Since humic acid (HA) and fulvic acid (FA) are ubiquitous in natural waters, it is necessary to study the effects of HA and FA on the adsorption of Gly onto NICO-D301. The HA and FA effects on Gly adsorption are shown in Fig. 6. As shown in Fig. 6, the presence of HA+FA and FA in aqueous solution led to obviously declined Gly adsorption onto NICO-D301. But the influence of HA on uptake capacity of Gly was slight. When the initial concentration of HA, FA and HA+FA in aqueous solution was 50 mg/L, the uptake capacity of Gly on NICO-D301 was decreased to 329.08, 314.61 and 322.50 mg/g, respectively. Whereas the initial concentration of HA, FA and HA+FA increased to 400 mg/g, the  $q_e$  values of NICO-D301 decreased to 313.95, 138.95 and 229.74 mg/g, respectively. From this point the presence of FA might have serious influence of Gly adsorption on NICO-D301, followed by HA+FA, finally HA, saying that the order of acid influence of the adsorption amount of Gly on NICO-D301 was  $FA > HA+FA > HA$ .

## Conclusions

D301 with higher loading amount of nano-iron and copper oxides exhibited higher Gly adsorption efficiency with capacity of 330.39 mg/g. The Gly adsorption capacity for NICO-D301 was relatively high at solution pH 3-5, and decreased with increasing solution pH from 5 to 12. The kinetic experiments showed that the adsorption of Gly onto NICO-D301 was rapid, and maximum adsorption capacities were achieved in 7h. The adsorption process was well fit by the pseudo-second-order model. The uptake of Gly decreased with increasing of FA concentration. HA had not obvious effect on Gly removal. The presence of major acid reduced Gly adsorption in the order of  $FA > HA+FA > HA$ .

## Acknowledgements

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