

SUPPORTING INFORMATION

Removal of chromium(VI) from wastewater using weakly and strongly basic magnetic adsorbents: Adsorption/desorption property and mechanism comparative studies

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Preparation of Pst-MIMCl magnetic microspheres

The Pst-MIMCl magnetic microspheres were synthesized using the substitution reaction followed by in-situ coprecipitation method. If the magnetic Pst microspheres were first prepared, the magnetic cores were easily dissolved by the anhydrous aluminum chloride in modification of the Friedel-Crafts reaction. In contrast, the in-situ coprecipitation method could effectively solve this problem, and the magnetic Fe_3O_4 nanoparticles were easily fabricated into the pores of the Pst microspheres through the coordination interaction between the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions and the tertiary amines on the N-methylimidazole (MIM).

Briefly, 5 g of Merrifield resin (Pst-Cl) was added into 50 mL of N,N-dimethylformamide (DMF) in a 250-mL flask, and stirred at room temperature for 2 h. Then 2 g of MIM was added, and the mixture was heated at 80 °C for 24 h. The resulting microspheres were washed several times with deionized water and ethanol to removal the residual MIM, and then immersed in 30 mL of a solution composed of 1.6 g (6 mmol) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1 g (5 mmol) of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in an ice bath. The mixture was then continuously evacuated under stirring until no further foaming was observed. The evacuation was stopped and the Pst-MIMCl microspheres were separated from the mixture by settlement. Next, the microspheres were dispersed in 50 mL of water at 85 °C in a flask equipped with a mechanical stirrer and a condenser. Ammonia hydroxide (10 mL) was added and the mixture was kept stirring for another 1 h. The Pst-MIMCl magnetic microspheres were obtained by washed several times with deionized water and ethanol and dried in a vacuum oven at room

temperature.

Preparation of CTS-GTMAC magnetic microspheres

1. Preparation of the CTS-GTMAC magnetic microspheres

(1) Synthesis of the magnetic silica nanoparticles

The magnetic silica nanoparticles were prepared using the chemical co-precipitation method followed by the sol-gel method. Briefly, the reaction system was firstly prepared by dissolving 2.33 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.86 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in 100 mL of deionized water at 85 °C with continuous nitrogen purging. Then 10 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ was quickly added into the medium with vigorous stirring. After a short time, 200 mg of sodium citrate was added and the medium was kept stirring for 30 min. The resulting Fe_3O_4 nanoparticles were separated by magnet and washed successively with deionized water and ethanol for several times. Next, the Fe_3O_4 nanoparticles were suspended into a mixture of 40 mL of ethanol, 10 mL of water and 1.2 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$. Then 0.4 mL of TEOS was added dropwise into the mixture and the solution was kept stirring for 12 h at room temperature. The magnetic silica nanoparticles were collected by magnet and washed several times with deionized water and ethanol.

(2) Synthesis of magnetic chitosan microspheres

The emulsion cross-linking method was used for the preparation of the magnetic chitosan microspheres. First, the chitosan solution was prepared by adding 5 g of chitosan powder in 200 mL of 5% acetic acid aqueous solution, and the dispersion medium was composed of 50 mL of mineral oil, 70 mL of petroleum ether and 2 mL of Tween-80. Next,

the magnetic silica nanoparticles (0.2 g) were immersed in 12 mL of the chitosan solution and then the mixture was slowly added into the dispersion medium under mechanical stirring of 1200 rpm at room temperature. Finally, 2 mL of glutaraldehyde was added into the medium and the reaction was kept for 2 h. The resulting microspheres were separated by magnet and washed consecutively with petroleum ether, ethanol and deionized water, which were designated as Fe₃O₄@SiO₂@CTS.

(3) Functionalization of magnetic chitosan microspheres

An amount of 2 g of the magnetic chitosan microspheres were submerged into a mixture of 50 mL of deionized water and 50 mL of EDA, and the mixture was kept stirring at 40 °C for 6 h. The obtained microspheres were washed with ethanol and deionized water several times and then suspended in 50 mL of 1% GTMAC solution. Moreover, the system was kept stirring for another 24 h at 60 °C. At last, the resulting CTS-GTMAC microspheres were collected and dried in a vacuum oven at room temperature.

Acid resistance of Pst-MIMCl and CTS-GTMAC

In order to character the acid resistance of Pst-MIMCl and CTS-GTMAC, the Fe₃O₄, Fe₃O₄@SiO₂, Pst-MIMCl and CTS-GTMAC were incubated in 15 mL of water at pH 2.0 for 24 h at 25 °C, and the Fe₃O₄ contents were maintained at 20 mg. The leaching Fe₃O₄ contents of Fe₃O₄, Fe₃O₄@SiO₂, CTS-GTMAC and Pst-MIMCl were measured as 6.64±0.39%, 0.27±0.03%, 0.08±0.01% and 1.64±0.13%, respectively. This result implied that the SiO₂ and polymer layers could effectively improve the acid resistance of the magnetic cores.

Figure S1

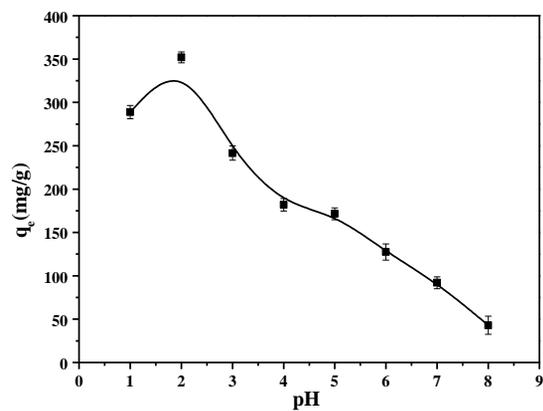


Fig. S1 Effect of the pH on Cr(VI) adsorption onto PGMA-PEI microspheres ($m=0.01$ g, $V=50$ mL, $C_0=150$ mg/L, $t=10$ min, $T=25$ °C)

Figure S2

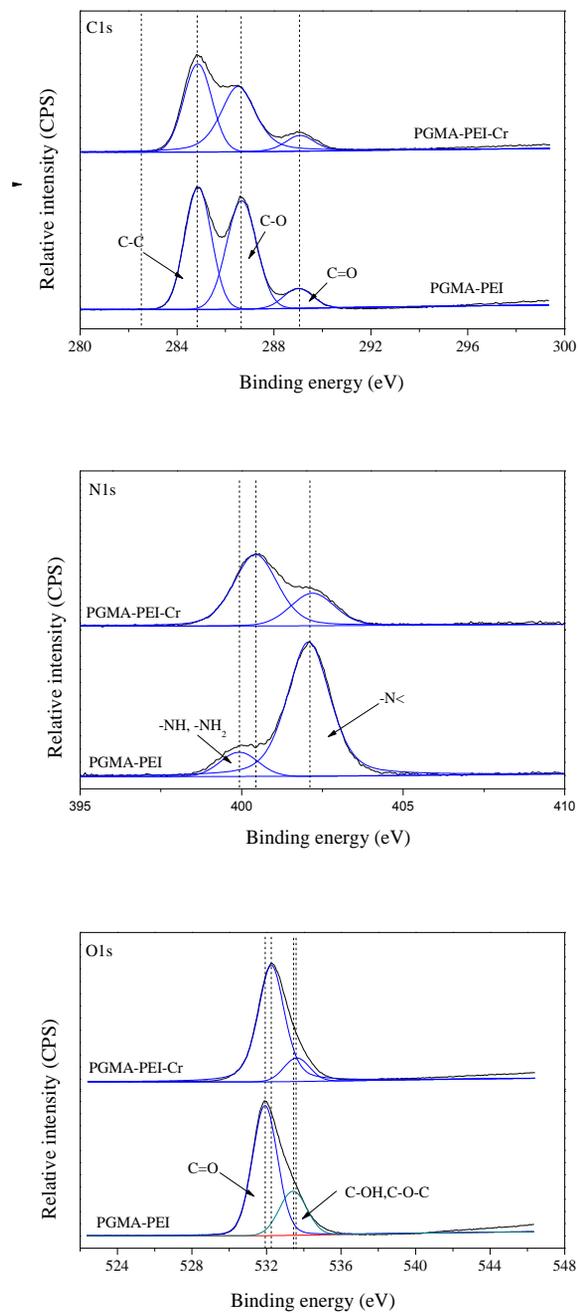


Fig. S2 XPS spectra of PGMA-PEI microspheres before and after Cr(VI) adsorption (adsorption conditions : m=0.01 g, V=50 mL, C₀=150 mg/L, pH=2.0, T=25 °C, t=10 min)

Figure S3

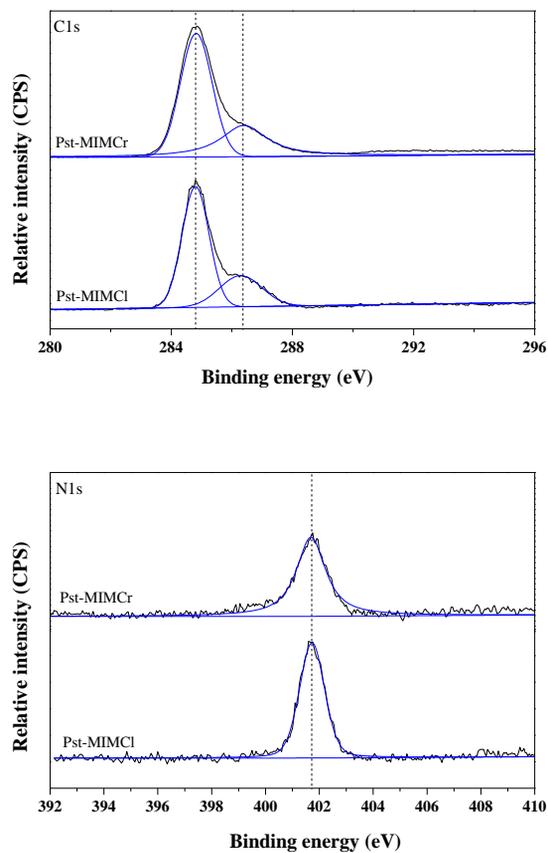


Fig. S3 XPS spectra of Pst-MIMCl microspheres before and after Cr(VI) adsorption (adsorption conditions :
 $m=0.03$ g, $V=48$ mL, $C_0=150$ mg/L, $pH=2.0$, $T=25$ °C, $t=30$ min)

Figure S4

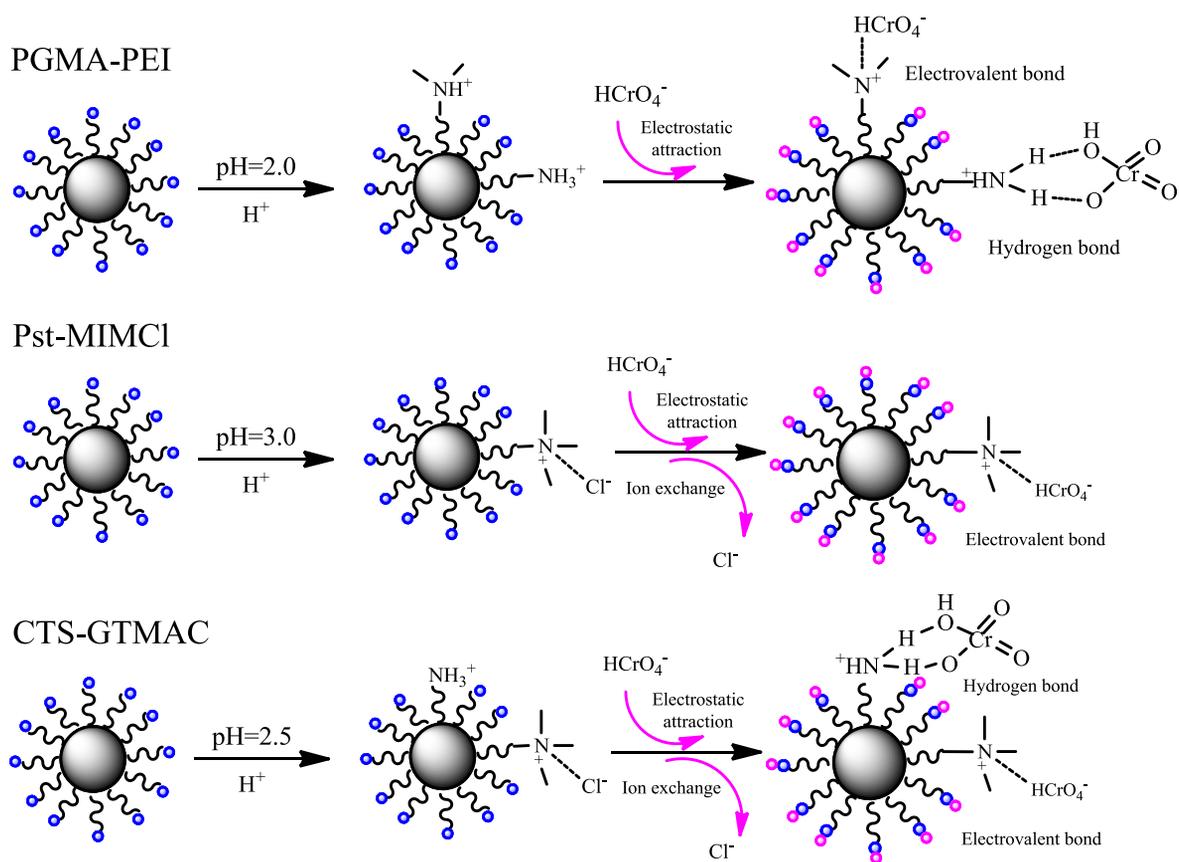


Fig. S4 Adsorption mechanisms of Cr(VI) adsorption onto PGMA-PEI, Pst-MIMCl and CTS-GTMAC magnetic microspheres.