Supplementary Data

Removal of copper and lead from aqueous solution by adsorption onto cross-linked chitosan/montmorillonite nanocomposites in the presence of hydroxyl–aluminum oligomeric cations: Equilibrium, kinetic, and thermodynamic studies

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FT-IR analysis

The types and functional groups of chitosan on CCPM were confirmed by a SHIMADZU FTIR-Affinity-1 spectrometer.

Figure S1. FT-IR spectrum of CCPM with the cross-linked chitosan-to-clay ratio of 0.45:1.

The FTIR spectrum obtained for CCPM was obtained (Fig. S1) to verify the presence of functional groups of chitosan. The major peaks for chitosan beads were observed around 3442 cm⁻¹ which was assigned to the stretching vibration of -OH groups. The peaks at 1650 and 1561 cm⁻¹ were attributed to the secondary amide C=O bond of the remaining acetamido groups and the -NH bending vibration of -NH₂ groups, respectively. The peak at 1416 cm⁻¹ can be assigned to -NH deformation vibration in -NH₂.

Determination of copper and lead

Reagents

dithizone, trichloromethane, sodium diethyldithiocarbamate (Na-DDTC), aqueous ammonia-solution, HNO_3 (65% to 68%), ammonium chloride and Triton X-100, were of analytical reagent grade. Copper and lead solutions of national standard (1 mg/mL) were purchased from Taiyuan Laibao Biological Technology Co., Ltd., China. Standard copper (10 $\mu\text{g/mL}$) and lead solutions (100 $\mu\text{g/mL}$) were prepared by suitable dilutions of copper and lead solutions (1 mg/mL) of national standard.

A Na-DDTC (100 $\mu\text{g/mL}$) stock solution was prepared by dissolving 0.2 g of Na-DDTC in a small volume of distilled water and diluted into a 100 mL volumetric flask with deionized water. The ammonium chloride–ammonia solution buffer was prepared by thoroughly mixing 5 g ammonium chloride with 35 mL of 25% aqueous ammonia solution. The 5% Triton X-100 solution was prepared by dissolving 5 mL Triton X-100 in a volume of deionized water and diluted into a 100 mL volumetric flask with deionized water. The dithizone stock solution (5 g/L) was prepared by dissolving 0.5 g dithizone in a volume of trichloromethane, diluted into a 100 mL volumetric flask with trichloromethane, and dissolved overnight. The dithizone solution was extracted by 25% aqueous ammonia solution 1:12 (v/v). The basic water phase was the freshly prepared dithizone color-developing agent.

Calibration curve

To determine copper content, 0.4 mL to 25 mL of each of the standard copper

solutions (10 µg/mL) was placed in one 100 mL volumetric flask. Na-DDTC solution (100 µg/mL) with an equivalent volume equal to the copper solution was then mixed. Subsequently, ammonia solution was added to adjust pH to 10 and diluted into a 100 mL volumetric flask with deionized water. The absorbance of Cu (DDTC)₂ was measured by a spectrophotometer at 450 nm against a reagent blank. The absorbance of each solution was recorded, and the results were calculated using Beer's Law. The calibration curve constructed by plotting the absorbance against the corresponding concentration was drawn, and the straight line adhered to the equation $A = 0.15466c + 0.03956$, with a correlation coefficient of (R^2) 0.99817.

To determine lead content, 0, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2, 2.25, 2.5, 2.75, and 3 mL of standard lead solutions (100 µg/mL) were placed separately in 100 mL beakers and then mixed with 35, 34.5, 34.25, 34, 33.75, 33.5, 33.25, 33, 32.75, 32.5, 32.25, and 32 mL of 1% HNO₃. Subsequently, 5 mL of 5% Triton X-100, 5 mL of ammonium chloride–ammonia solution buffer, and 5 mL of dithizone color-developing agent were added. The absorbance was measured by a spectrophotometer at 472 nm against a reagent blank. The calibration curve adhered to the equation $A = 0.05890c + 0.28760$, $R^2 = 0.99099$.

Effect of cross-linked chitosan-to-clay ratios on Cu (II) or Pb (II) adsorption

The nanocomposites with different cross-linked chitosan to clay ratios of 0.20:1, 0.30:1, 0.45:1, 0.60:1, and 1.20:1 exhibited different metal removal efficiencies. Figure S1 shows that with the increase in the cross-linked chitosan-to-clay ratio, both the removal efficiency and the adsorption capacity of CCPM on the two metal ions increased and then decreased. Therefore, adsorption of the two metal ions was significantly affected by the ratio of cross-linked chitosan to MMT. The nanocomposite with the cross-linked chitosan-to-clay ratio of 0.45:1 was suitable in the Cu (II) or Pb (II) adsorption system. Thus, it was selected as the optimum ratio and applied in the following experiment.

Figure S2. Effect of modification ratio on the adsorption capacity and removal efficiency (inset) of CCPM for Cu (II) and Pb (II) [C_0 : Cu (II) 100 mg/L, Pb (II) 100 mg/L; adsorbent dosage: Cu (II) 10 g/L, Pb (II) 5 g/L; pH: Cu (II) 6.5, Pb (II) 6; contact time: 2 h; temperature: 298 K].