

Supplementary Materials

Core-shell Fe₃O₄@zeolite NaA as an Adsorbent for Cu²⁺

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Received: 7 October 2020; Accepted: 3 November 2020; Published: date

SI Supporting Materials and Methods

Batch Adsorption Experiments

S1.Preparation of Cu²⁺ Solutions

Prepared a standard Cu²⁺ stock solution (500 mg/L) by dissolving Cu(SO₄)₂·5H₂O in a beaker. The solution was then diluted to the desired concentration using deionized water.

S2.Adsorption Study

All adsorption experiments were performed in a batch mode using a shaking table (MPS-1500, Ningbo, zhejiang province, China) at a controlled temperature. The pH of the solution was adjusted to the desired value by adding negligible volume of 0.1 M NaOH and 0.1 M HCl solution. The determination of pH value is measured by SMART PH818 PH meter. After the adsorption test, the sample was immediately filtered through a syringe filter (0.45 μm syringe filter, PP filter medida, Yuecheng, China), and the remaining Cu²⁺ concentration in the supernatant was measured by inductively coupled plasma spectrometer (ICP- OES) analysis (8300, PerkinElmer, USA). The adsorption experiment was performed in a reciprocating water bath shaker at a shaking speed of 170rpm. The adsorption capacity (Q_e, mg/g) and adsorption efficiency of the adsorbents were calculated using the following Equations (S1) and (S2) [1]:

$$Q_e = \frac{C_0 - C_e}{M} \times V \quad (S1)$$

$$R_{\text{removal}\%} = \frac{C_0 - C_e}{C_0} \times 100 \quad (S2)$$

Where Q_e is the adsorption capacity (mg/g); C₀ is the initial Cu²⁺ concentration (mg/L); C_e is the final Cu²⁺ concentration (mg/L); M (g) is the weight of the adsorbent used and V (L) is the volume of the Cu²⁺ solution. R_{removal%} is the removal rate of Cu²⁺ by the adsorbent; Each experiment was repeated three times to obtain average results.

Adsorption Kinetics Study

The knowledge of adsorption kinetics is important information for designing batch adsorption systems. To examine the adsorption kinetics of the adsorbent for Cu^{2+} , the Lagergren pseudo-first-order and pseudo-second-order kinetic models were examined [2].

(1) Lagergren pseudo-first-order kinetic model:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (\text{S3})$$

(2) Lagergren pseudo-second-order kinetic model:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (\text{S4})$$

where Q_e is the amounts of adsorption at equilibrium, mg/g; Q_t is the amounts of adsorption at time t , mg/g; k_1 is the first order rate constant, min^{-1} ; k_2 is the second order rate constants, min^{-1} .

Adsorption Isotherm Study

The liner form of Langmuir adsorption isotherm is one of the most famous well-adopted models used to describe the solid phase adsorption systems [3].

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{K_L Q_{\max}} \quad (\text{S5})$$

$$R_L = \frac{1}{1 + K_L C_0} \quad (\text{S6})$$

Where $Q_{\max}$ is the Langmuir maximum adsorption capacity (mg/g), and K_L is the Langmuir binding constant. Where C_0 and K_L are the initial concentration of arsenic and Langmuir isotherm constant. If the value of $0 < R_L < 1$, it represents favourable adsorption.

The Freundlich model indicates the heterogeneity of the adsorbent surface and considers multilayer adsorption. The linear form of Freundlich adsorption model is as follows [4]:

$$\ln Q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (\text{S7})$$

Where K_f and $1/n$ are Freundlich constants, related to adsorption capacity and adsorption intensity (heterogeneity factor) respectively. The values of K_f and $1/n$ were obtained from the slope and intercept of the linear Freundlich plot of $\ln Q_e$ versus $\ln C_e$.

The Temkin model is a modification equation of the Langmuir model. The adsorption enthalpy declined linearly with the increase of adsorption amounts. The Temkin model is described by equation S8:

$$Q_e = B_1 \ln K_t + B_1 \ln C_e \quad (\text{S8})$$

where B_1 and K_t are constants related to adsorption enthalpy and capacity of the adsorbent.

Thermodynamic Study

Using the slope and intercept of the plot the $\ln K_d$ versus $1/T$ is presented in Equation 9, the enthalpy change (ΔH^0) and entropy change (ΔS^0) can be calculated. $T(K)$ is the Kelvin temperature. $R(8.314J/(mol \cdot K))$ is the universal gas constant. The Gibbs free-energy change of the sorption of Cu^{2+} ions using adsorbent is given using Equation 9:

$$K_d = \frac{Q_e}{C_e}$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (S9)$$

The standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0) was calculated using following equation [5]:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (S10)$$

Where (ΔH^0) is standard enthalpy change (KJ/mol) and (ΔS^0) is standard entropy change (KJ/mol K).

Table S1. XRF analyze of $Fe_3O_4@SiO_2$ (w %).

Items	Content(w %)
Fe_3O_4	47.003
SiO_2	51.663

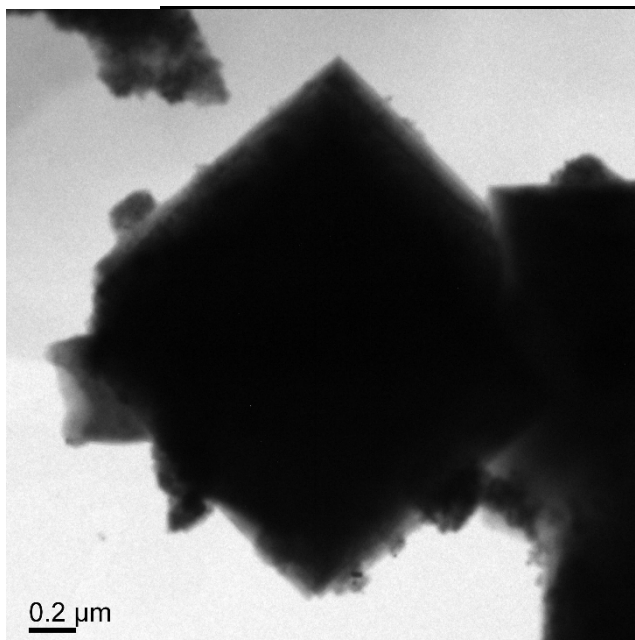


Figure S1. TEM image of magnetic zeolite NaA.



Figure S2. Separation ability test of $\text{Fe}_3\text{O}_4@\text{zeolite NaA}$.

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