Supporting Information

Enhanced catalytic ability of chitosan-Cu-Fe bimetal complex for the removal of dyes in aqueous solution

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Text S1. Preparation of Chitosan-Cu and Chitosan-Fe Complexes

The preparation process of catalyst chitosan-Cu complex was done by modifying the literature procedure described by Kucherov and co-workers. Chitosan (1 g) was slowly dissolved in 50 mL water containing 0.4 mL acetic acid at room temperature and stirred until chitosan was dissolved. Then, 50 mL of 0.1 mol/L CuSO$_4$·5H$_2$O was added into the dissolved chitosan. The mixture was stirred for 30 min until resulting in the coagulation of chitosan-Cu into gel. The chitosan-Cu complex was repeatedly washed with water until neutral pH and dried at 80°C. Hereafter chitosan-Cu will be mentioned as CS-Cu for simplicity’s sake.

Chitosan-Fe complex was prepared by modifying the literature procedure. Chitosan powder (1.0 g) was dissolved in 0.1 mol/L FeCl$_3$ aqueous solution (50 mL), and the mixture was stirred at room temperature for 4 h. Chitosan-Fe complex precipitation was obtained after the addition of ethanol and then the solid was washed with ethanol to remove an excess of FeCl$_3$ and finally dried at 80°C. It was then placed in ethanol solution containing 5% of glutaraldehyde for 12 h, according to the chemical crosslinking of chitosan with glutaraldehyde occurs by Schiff’s reaction. From now on chitosan-Fe is referred as CS-Fe for the sake of simplicity.

Text S2. Kinetic Models

The pseudo-first-order rate model,

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

(1)

and the second-order rate model,
where $q_e$ and $q_t$ are the amounts of dye adsorbed (mg/g) at equilibrium and at different intervals, respectively; $k_1$ (1/min) and $k_2$ (g/mg·min) are the pseudo-first-order and second-order rate constants; and $h$ represents the initial adsorption rate (mg/g·min).

Text S3. Isotherm Models

The Langmuir isotherm was originally proposed to describe the adsorption of gas molecules onto metal surfaces. The model assumes uniform energy of the adsorption onto the surface and no migration of the adsorbate in the plane of the surface. It is expressed as

$$q_e = \frac{abC_e}{1 + bC_e}$$

where $q_e$ is the amount of dye adsorbed at equilibrium (mg/g) and $C_e$ is the adsorbate concentration at equilibrium in aqueous solution (mg/L). The Langmuir isotherm parameters are $a$ and $b$. The capacity of the adsorbent can be evaluated by $a$, and the parameter $b$ includes various physical constants.

The Freundlich isotherm describes heterogeneous systems on the surfaces with non-energetically equivalent sites. The equation can be written as follows:

$$q_e = K_f C_e^{1/n}$$

where $K_f$ is the Freundlich constant, which is indicative of the extent of adsorption, and $1/n$ is the heterogeneity factor, an indicator of adsorption effectiveness.
Another useful equation is the Langmuir-Freundlich isotherm, which is based on the generalized Langmuir and generalized exponential isotherms and is the most promising extension of the Langmuir and Freundlich isotherms. It is expressed as

$$q_e = \frac{q_m (K_{lf} C_e)^{1/v}}{1 + (K_{lf} C_e)^v}$$

where $q_m$ is the maximum adsorption (mg/g), $K_{lf}$ is the Langmuir-Freundlich constant (L/mg)$^{1/v}$, and $v$ is the Langmuir-Freundlich heterogeneity constant. The Langmuir-Freundlich isotherm is essentially the Freundlich isotherm approaching a maximum at high concentrations.

**Literature Cited**


Table S1. Parameters of kinetic study for dyes adsorption onto chitosan-Cu-Fe complex.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Initial Concentration (mg/L)</th>
<th>Pseudo first-order equation</th>
<th>Pseudo second-order equation</th>
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<tr>
<td></td>
<td>q_e (mg/g)</td>
<td>K_f (1/min)</td>
<td>R^2</td>
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<tr>
<td>CS-Cu-Fe-1</td>
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