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 [1]. 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 $CuSO_4·5H_2O$ 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. Here after chitosan-Cu will be mentioned as CS-Cu for simplicity's sake.

Chitosan-Fe complex was prepared by modifying the literature procedure [2]. 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,

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{1}$$

and the second-order rate model,

1 $$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t, \quad h = k_2 q_e^2,$$ (2)

2 where q_e and q_t are the amounts of dye adsorbed (mg/g) at equilibrium and at

3 different intervals, respectively; k_1 (1/min) and k_2 (g/mg·min) are the pseudo-first-

4 order and second-order rate constants; and h represents the initial adsorption rate

5 (mg/g·min).

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7 **Text S3. Isotherm Models**

8   The Langmuir isotherm was originally proposed to describe the adsorption of gas

9 molecules onto metal surfaces. The model assumes uniform energy of the adsorption

10 onto the surface and no migration of the adsorbate in the plane of the surface. It is

11 expressed as

12 $$q_e = \frac{abC_e}{1 + bC_e}$$ (3)

13   where q_e is the amount of dye adsorbed at equilibrium (mg/g) and C_e is the

14 adsorbate concentration at equilibrium in aqueous solution (mg/L). The Langmuir

15 isotherm parameters are a and b. The capacity of the adsorbent can be evaluated by a,

16 and the parameter b includes various physical constants.

17   The Freundlich isotherm describes heterogeneous systems on the surfaces with

18 non-energetically equivalent sites. The equation can be written as follows:

19 $$q_e = K_f C_e^{1/n}$$ (4)

20   where K_f is the Freundlich constant, which is indicative of the extent of

21 adsorption, and $1/n$ is the heterogeneity factor, an indicator of adsorption

22 effectiveness.

1   Another useful equation is the Langmuir-Freundlich isotherm, which is based on

2 the generalized Langmuir and generalized exponential isotherms and is the most

3 promising extension of the Langmuir and Freundlich isotherms. It is expressed as

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

4   (5)

5 where q_m is the maximum adsorption (mg/g), K_{lf} is the Langmuir-Freundlich

6 constant $(L/mg)^{1/v}$, and v is the Langmuir-Freundlich heterogeneity constant. The

7 Langmuir-Freundlich isotherm is essentially the Freundlich isotherm approaching a

8 maximum at high concentrations.

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Literature Cited

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

2 complex.

Adsorbent	Initial Concentration (mg/L)	Pseudo first-order equation			Pseudo second-order equation		
		q_e (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	K_2 (g/mg·min)	R^2
CS-Cu-Fe-1	50	39.45	0.29	0.9731	53.79	0.01	0.9731
	100	83.07	0.93	0.9697	96.85	0.02	0.9981
	200	115.19	0.58	0.9229	125.62	0.004	0.9843
	300	193.89	0.38	0.9687	291.97	0.001	0.9859

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