ELECTRONIC SUPPLEMENTARY MATERIAL

Selective Crystal Growth of Magnesium Hydroxide via Solvent Control for Dye Adsorption

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Experimental Section

Materials

$MgCl_2 \cdot 6H_2O$, $NH_3 \cdot H_2O$, anhydrous ethanol, ethylene glycol (Xilong Chemical Company), NaOH (Beijing Chemical Industry Co. ltd), Congo red (Sinopharm Chemical Reagent Co. ltd) were used as purchased without further purification. The deionized was used in all the experimental processes.

Synthesis of magnesium hydroxide with different ratios of ethanol/water

In the molar ratio 1:2 ($MgCl_2 \cdot 6H_2O$ to ammonia), 40.66 g of $MgCl_2 \cdot 6H_2O$ was dissolved in 100 mL deionized water as salt solution (2 mol/L), and 27.248 g of ammonia were dissolved in 100 mL deionized water as base solution. Then, these two solutions were rapidly mixed to generate a large number of nuclei by using a

rotating liquid film reactor at room temperature. A quantity of anhydrous ethanol was added to the slurry stirred in the nucleation of a volume fraction of 5%, 10%, 25%, and 50%. The mixed slurry was transferred to a high pressure reactor for crystallization at 80 ℃ for 6 h, followed by cooling to room temperature. After washing with deionized water for about 4~6 times, the obtained precipitate was dried in a drying oven at 60 ℃ for 8 h to obtain magnesium hydroxide.

Synthesis of magnesium hydroxide with different ratios of ethylene glycol/water

Similar to the synthesis method above, the ethanol was replaced with ethylene glycol, other conditions remained unchanged, and the magnesium hydroxide samples were synthesized with the ratio of ethylene glycol being 5%, 7.5%, 10%.

Characterizations

The crystal structure of magnesium hydroxide was analyzed by X-ray powder diffractometer (Rigaku, D/max-UItima III) using Cu target Kα rays at 40 kV and 30 mA, scanning step of 5-70° and scanning speed of 10°/min. The surface morphology of magnesium hydroxide was analyzed using a scanning electron microscope (ZEISS, Supra 55). The specific surface area of magnesium hydroxide was analyzed using a fully automated specific surface area and pore size analyzer (Quandasorb SI, Kantar Instruments, USA). Before testing, 0.1 g of sample was weighed and placed in a sample tube and degassed under vacuum for 6 h at 120 °C. The secondary particle size distribution was analyzed using a laser particle size tester (Mastersize 2000, Malvern, UK). The samples were ultrasonicated for 5 min in a cell pulverizer with a power of 900 W. The zeta potential of magnesium hydroxide was tested by a particle size analyzer (Malvern, model: Zetasizer Nano ZS90). The refractive index of the particles of $Mg(OH)_2$ was 1.580 and the absorptivity was 0.01. The zeta potential of $Mg(OH)_2$ was measured by the same analyzer (Malvern, model: Zetasizer Nano ZS90).

Adsorption experiment

A certain concentration of Congo red solution was prepared as the simulated dye wastewater, and the pH of the solution was adjusted with sodium hydroxide solution and dilute hydrochloric acid. A certain amount of magnesium hydroxide powder and 100 mL of the simulated dye wastewater were added to a 250 mL conical flask, and the adsorption was carried out by shaking in a water-bath shaker. After reaching the equilibrium of the adsorption the suspension was centrifuged for 3 min at 4000 rad/min, and the supernatant was taken as the reference solution. The absorbance of the solution was measured at 500 nm. The absorbance of the solutions was tested using a UV-Vis spectrophotometer (Shimadzu, Japan, UV-2501PC). The content of the substance was calculated by measuring the absorbance at the characteristic wavelength of the sample.

Adsorption isotherm

In order to investigate the thermodynamic behavior of the adsorption process of magnesium hydroxide on CR, the Langmuir and Freundlich models were chosen to fit the experimental data linearly in this experiment.

Langmuir model is a monomolecular layer adsorption process, homogeneous adsorption, , and the adsorption equilibrium reached is a dynamic equilibrium. Its linear expression is as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L \times q_m} + \frac{C_e}{q_m}$$

where K_L is the adsorption equilibrium constant, $q_e$is the equilibrium adsorbed amount of the adsorbent (mg/g), C_e is the concentration of the solute at the time of adsorption equilibrium (mg/L), and q_m is the maximum adsorbed amount (mg/g).

The Freundlich model is based on a solid surface that is inhomogeneous and has different

adsorption sites and adsorption energies. Its linear expression is as follows:

$$lgq_e = lgK_F + \frac{1}{n}lgC_e$$

where K_F and n are constants in the model, K_F is related to the adsorption efficiency, n reflects the strength of the adsorption effect, C_e is the concentration of the solute at the adsorption equilibrium (mg/L), and q_e is the equilibrium adsorption amount of the adsorbent (mg/g).

Adsorption kinetics

In order to investigate the kinetics of the adsorption process, the adsorption process of magnesium hydroxide on Congo red is fitted by the quasi-primary and quasi-secondary kinetic equations.

The linear expression of the quasi-primary kinetic model is as follows:

$$lg(q_e - q_t) = lgq_e - k_1 t$$

where q_e is the adsorbed amount at adsorption equilibrium (mg/g), k_1 is the first-order kinetic adsorption constant, and q_t is the adsorbed amount of Congo red by magnesium hydroxide at time (mg/g). Fitting the curve graphically to t with $lg(q_e - q_t)$ gives k_1

The linear expression of the quasi-secondary kinetic model is as follows:

$$\frac{t}{q_e} = \frac{1}{K_L q_e^2} + \frac{t}{q_e}$$

where q_e is the amount adsorbed at adsorption equilibrium (mg/g), k_2 is the first-order kinetic adsorption constant, and q_t is the amount of Congo red adsorbed by magnesium hydroxide at time (mg/g). Fitting the curve graphically with t/q_t against t gives k_2.

Supplementary figures

Table S1 Particle size results of magnesium hydroxide obtained different volume ratio of ethanol

	D(50)/μm	**D(90)/μm**
0%	0.932	2.017
5%	0.076	0.541
10%	0.075	0.477
25%	0.075	0.403
50%	0.061	0.378

Table S2 Particle size results of magnesium hydroxide obtained different volume ratio of ethylene glycol

	D(50)/μm	**D(90)/μm**
0%	0.932	2.017
5%	0.061	0.308
7.5%	0.050	0.376
10%	0.050	0.377

Table S3 Fitting parameters of kinetic model for CR adsorption on magnesium hydroxide: a. I_{001}/I_{101} = 1.258, b. I_{001}/I_{101} = 1.023, c. I_{001}/I_{101} = 0.822

$Mg(OH)_2$	$q_{e,\ exp}$ （mg/g）	Pseudo-first-order model			Pseudo-second-order model		
		k_1 (min^{-1})	q_e (mg/g)	R^2	$k_2\times10^{-4}$ (min^{-1})	q_e (mg/g)	R^2
a	46.762	0.0191	34.752	0.955	7.992	45.579	0.997
b	45.744	0.0192	39.901	0.920	8.977	44.131	0.994
c	47.359	0.0159	10.392	0.216	12.154	43.802	0.976