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RESEARCH ARTICLE

Morphology selective construction of β-cyclodextrin functionalized Fe_3O_4-Bi_2WO_6 nanocomposite with superior absorptivity and visible-light-driven catalytic activity

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Electronic Supplementary Material

Experimental details

1. *Characterization of the photocatalysts*

X-ray diffraction (XRD) diagrams to estimate the crystalline phase composition of the samples were measured using Bruker AXS D8-Advance diffractometer fitted with a (Cu Kα λ = 1.5418 Å) radiation tube. The data were analysed on PANalytical X'Pert High Score Plus 2.2 software. The morphologies and structures were observed by scanning electron microscopy (SEM, KYKY-EM3200) and high-resolution transmission electron microscopy (HRTEM, 300 kV Philips CM30). Fourier transform infrared (FTIR) spectra in the range of 400-4000 cm-1 were recorded in transmission mode using (Thermo Nicolet 8700), the powder samples were ground with KBr and compressed into a pellet prior to analysis. X-ray photoelectron spectroscopy (XPS) was recorded on a (VG MultiLab 2000) system using Al Kα monochromatic. BET surface area and porosity measurements were performed on a (Belsorp Max) instrument. UV-Vis absorption spectra were measured using a UV-Vis double-beam spectrophotometer (PG Instruments T80+). The magnetic properties of the composites were measured using a vibrating sample magnetometer (VSM, Lakeshore Model 7300 series). Finally, energy-dispersive spectrum (EDS) to determine the existing elements was performed on (Mira 3-XMU Simaging Detectors).

2. *Adsorption measurements*

Since the adsorption of pollutant on the catalyst surface is a key factor to commence the photocatalytic mediated degradation and in order to inspect the role of embedded β-CD in facilitating the adsorption process, the adsorption capability of CD-F-BWO was studied and compared with that of F-BWO and bare BWO. For that, batch equilibrium experiments in the dark were performed by dispersing a fixed amount of each photocatalyst (10 mg) in 50 mL aqueous solutions of differing SY initial concentrations in the range 16-65 mg L^{-1}. The suspensions were then magnetically stirred under adjusted atmospheric temperature (25±2 °C). In the meantime, samples were withdrawn at different time intervals until the equilibrium reached and residual SY concentrations were analysed to estimate the removal efficiency (R%) and adsorption capacity q_t (mg g^{-1}) as follows:

$$R\% = \frac{(A_0 - A_t)\times 100}{A_0} = \frac{(C_0 - C_t)\times 100}{C_0} \qquad (1)$$

$$q_t = \frac{(C_0 - C_t)\times V}{m} \qquad (2)$$

A_0 and C_0 are the initial absorbance and concentration of SY, respectively, while A_t and C_t are the absorbance and concentration after (t) min of stirring. Kinetics study was accomplished to further describe the exact relationship between the adsorption rate and SY concentration. Pseudo-first order and pseudo-second order kinetic models were adopted to examine the experimental data and predict the adsorption kinetic. These models are expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

Where, q_e (mg g^{-1}) is the amount of SY adsorbed by the catalyst at equilibrium time (equilibrium adsorption capacity), k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the equilibrium rate constants of pseudo-first order and pseudo-second order adsorption kinetics, respectively. For the pseudo-first order model, plot of $\ln(q_e\text{-}q_t)$ versus t of different concentrations was used to determine the k_f and q_e. On the other hand, values of k_2 and q_e were calculated from the intercept and slope of t/q_t versus t plot for the pseudo second order kinetic model. Furthermore, the Langmuir and Freundlich isotherms were used to describe the relationship between the adsorbed amount of SY (q_e, mg g^{-1}) and its concentration (C_e, mg L^{-1}) at equilibrium time for a better understanding of SY adsorption behavior onto BWO and its composites. Langmuir and Freundlich isotherms are represented by the following equations, respectively:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \qquad (5)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (6)$$

Where, Q_m is the maximum Langmuir adsorption capacity (mg g^{-1}), K_L is the Langmuir equilibrium adsorption constant (L mg^{-1}), K_F is the Freundlich capacity factor (mg g^{-1}(L $mg^{-1})^{1/n}$) and (1⁄n) is the Freundlich intensity parameter. The linear plot of C_e/q_e versus C_e suggests the applicability of Langmuir isotherm, whereas the linear plot of log q_e versus log C_e suggests the applicability of Freundlich isotherm. The time needed to reach equilibrium was chosen based on the kinetic study.

3. *Photocatalytic reactivity measurements*

Photocatalytic decomposition of SY under ambient conditions was performed to determine the optimal procedure for Bi_2WO_6 synthesis and to evaluate the functionalization effect on the photocatalytic reactivity. The photocatalytic experiments were conducted in a home-made photoreactor described in details in our previous work and shown in Fig. S1 [1]. The catalyst was added at 10 mg dose into 50 mL of substrate solution with concentrations 10-20 mg L^{-1}. Prior to the reaction, the suspension was kept in the dark for 60 min to reach adsorption-desorption equilibrium. The suspension was then continuously irradiated by a 650 W halogen lamp. At given time intervals, 3 mL aliquots were collected and centrifuged. The extent of SY degradation was established by monitoring the absorbance of the dye treated solutions using UV-Vis spectrophotometry at 482 nm using eq (1).

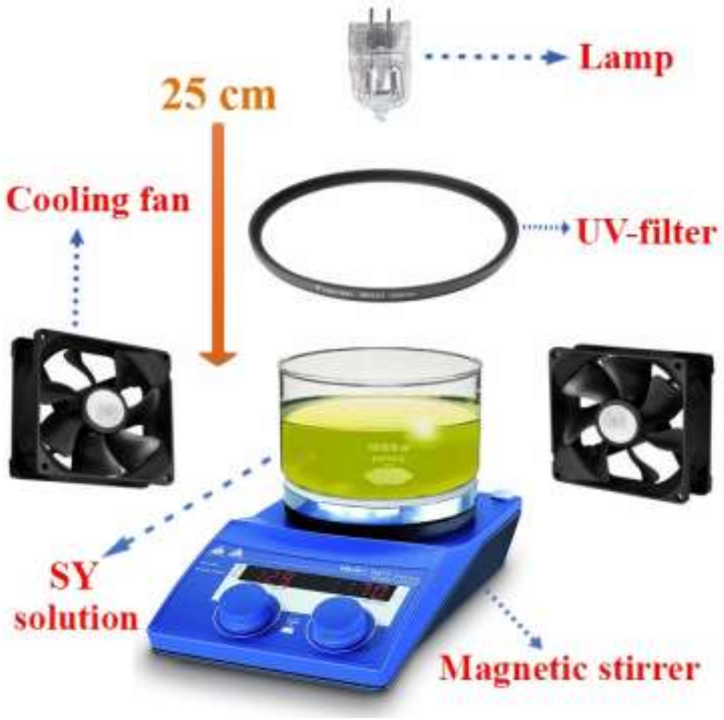

Fig. S1. Photoreactor system

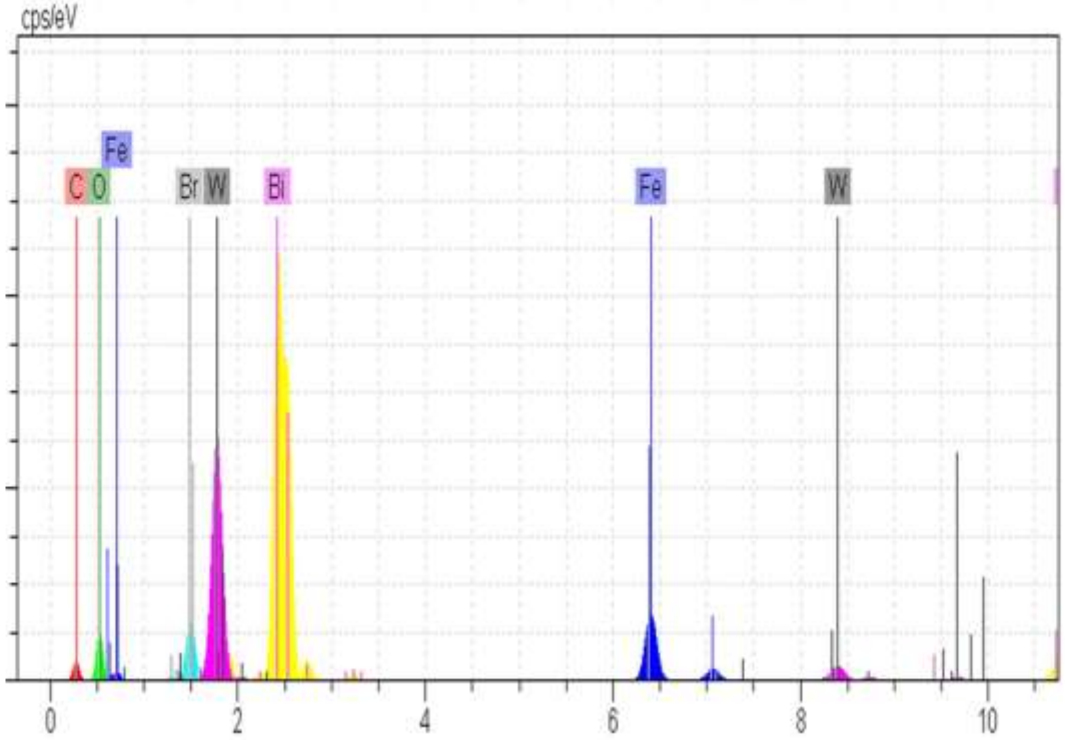

Fig. S2. EDS spectrum of CD-F-BWO

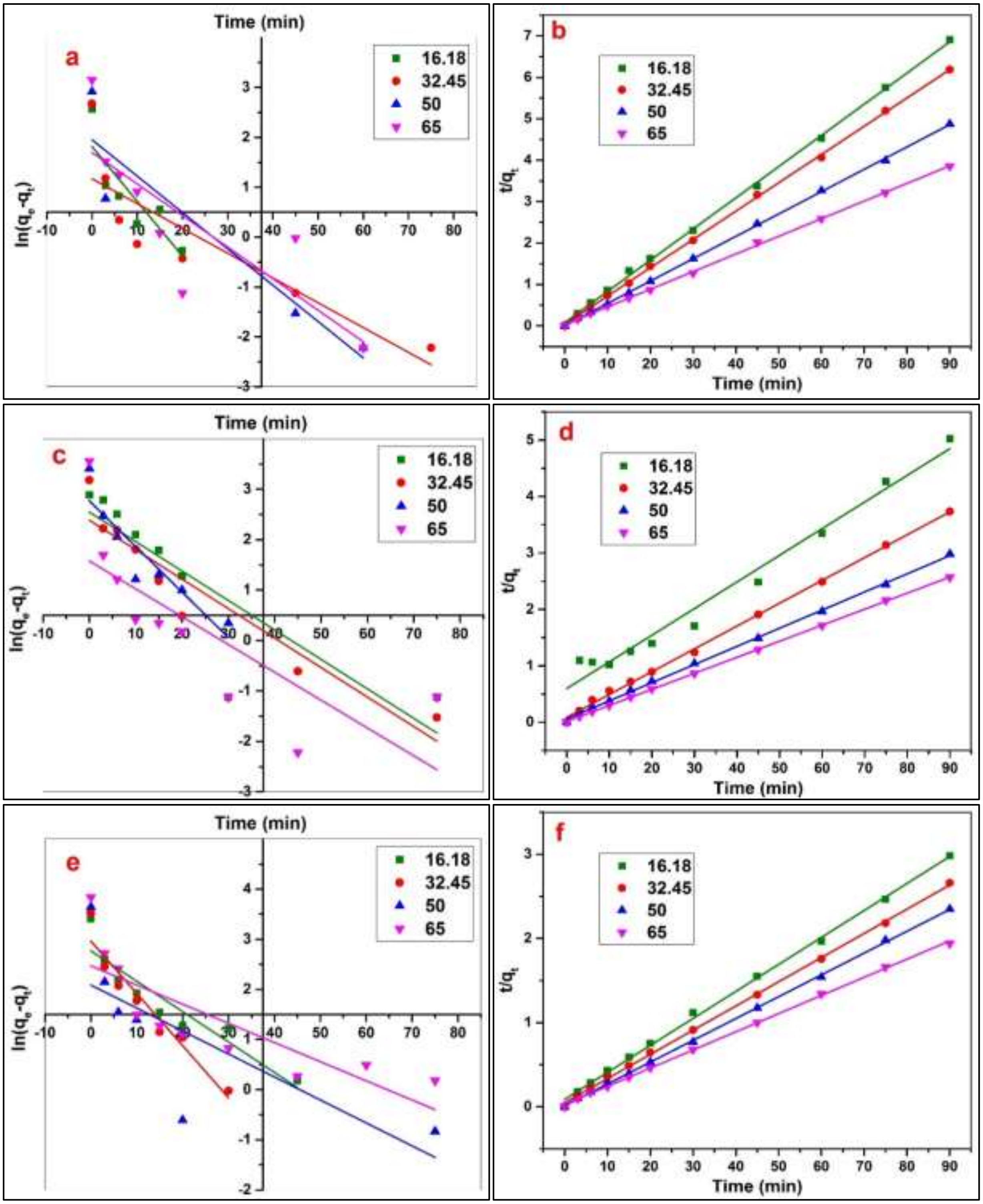

Fig. S3. Pseudo-first order and pseudo-second order adsorption kinetics of SY over (a and b) BWO; (c and d) F-BWO; (e and f) CD-F-BWO;

Table S1. The kinetic parameters of SY adsorption calculated from the two models

	SY (mg L^{-1})	q_e (Exp)	Pseudo-first order			Pseudo-second order		
			$q_{e\ (1)}$	$K_1(*10^{-3})$	R^2	$q_{e\ (2)}$	$K_2(*10^{-3})$	R^2
BWO	16	13.03	6.161	110.0	0.734	13.28	72.32	0.999
	32	14.55	3.223	49.76	0.753	14.64	128.5	0.999
	50	18.46	7.053	72.94	0.882	18.51	194.4	0.999
	65	23.33	5.476	63.35	0.673	23.47	57.61	0.999
F-BWO	16	17.91	12.80	54.82	0.754	21.18	3.731	0.930
	32	24.10	10.88	58.42	0.905	24.69	19.07	0.998
	50	30.19	15.94	90.38	0.849	31.05	18.09	0.999
	65	35.06	4.840	55.21	0.600	35.21	59.30	0.999
CD-F-BWO	16	30.18	15.96	60.60	0.884	31.15	11.76	0.998
	32	33.84	19.34	104.1	0.928	34.72	17.64	0.999
	50	38.31	8.050	45.86	0.583	38.61	57.82	0.999
	65	46.35	11.81	38.25	0.683	46.29	17.02	0.999

Table S2. Parameters for Langmuir and Freundlich isotherm models at different concentrations

Isotherm	Langmuir isotherm			Freundlich isotherm		
Constants	Q_m	K_L	R^2	K_f	n	R^2
BWO	30.48	0.040	0.938	4.675	2.71	0.862
F-BWO	48.07	0.041	0.974	5.843	2.29	0.993
CD-F-BWO	51.81	0.095	0.955	17.17	4.38	0.865

References

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