Electronic Supplementary Information (ESI)

Selectively photodegrading and then backfilling for regeneration of the inorganic - organic hybrid composite: Fe_3O_4@C_{18}ADB@Zn_2SiO_4 capturing organic pollutants from aqueous solution

Zheng-Yong Chen, Hong-Wen Gao* and Ya-Yuan He

Experimental details

Synthesis of the Fe_3O_4@C_{18}ADB@Zn_2SiO_4 hybrid composite

1.5 g of commercial ferric oxide particles (content >99.5%, spherical particle size <20 nm, Aladdin Reagents Co., China) was dispersed into 25 ml of 35% (v/v) ethanol and mixed for 10 min with an ultrasonic fragmentation device (Model JY92-II, Xinzhi Biotechnol. Co, Ltd, Ningbo, China). 15 g of C_{18} alkyl dihydroxyethyl betaine (Shanghai Promise song industry, China) was dissolved in 500 ml of 35% (v/v) ethanol aqueous solution and it was added under vigorous stirring for 10 min. By mixing thoroughly with 50 ml of 20% (w/v) zinc nitrate, 100 ml of 5% (w/v) sodium silicate was added rapidly under stirring. After stationarily aging for 24 h at 40 ^oC, the hybrid composite was washed repeatedly with deionized water to remove the excessive C_{18}ADB. The Fe_3O_4@C_{18}ADB@Zn_2SiO_4 suspension liquid was used to adsorb dyes and EDCs and the dry- Fe_3O_4@C_{18}ADB@Zn_2SiO_4 ground into powder for characterization of structure and morphology. The Fe_3O_4@C_{18}ADB@Zn_2SiO_4 hybrid composite was separated with a magnet rod for 5 min.

Characterization of the material structure and morphology

The IR spectra were measured with a Fourier transform infrared spectrometer (Model NICOLET 5700, Thermo Electron Co., USA) to indicate C_{18}ADB embedded into the hybrid materials. The heat weight change of the materials was performed with a thermal gravimetric analyser (Model TGA/SDTA Q600, Mettler Toledo Co.). A scanning electronic microscopy (SEM) (Model Quanta 200 FEG, FEI Co., USA) was used to measure the size and shape of the hybrid sorbents. A transmission electron microscopy (TEM) (Model TECNAI G2, S-TWIN, FEI Co., USA) was used to characterize the morphology of the Fe_3O_4@C_{18}ADB@Zn_2SiO_4 hybrid composite. A ζ-potential instrument (Zetasizer Nano Z, Malvern, UK) was used to determine the surface potential of the sorbents. Magnetic properties were measured at room temperature by vibrating sample magnetometry (Model Lakeshore 7407, USA). The surface area of the materials was measured with a surface area and porosimetry analyzer (Model ASAP2020, Micromeritics Co., USA). The small-angle X-ray diffraction (SAXRD) (Model D/Max-2550 PC, Japan) was recorded using CuK radiation at a voltage of 30 kV and current of 50 mA. The elemental analysis device (Model Vario EL Ⅲ, Germany) used to determine C, N and H content of hybrid composite gradually decreased with increasing of the photocatalytic time. The dye-Fe_3O_4@C_{18}ADB@Zn_2SiO_4 hybrid sludge was degraded with a photochemical reaction instrument (Model BL-GHX-V, Shanghai Bilon Experiment Co., Ltd, China) and an inverted fluorescence microscopy (Model TE2000-U, Nikon, Japan) to take the photos of sludge.

Adsorption of dye to the Fe_3O_4@C_{18}ADB@Zn_2SiO_4 material

0.05% (w/v) of the Fe_3O_4@C_{18}ADB@Zn_2SiO_4 hybrid composite was added into congo red and reactive brilliant red X-3B from 0.5 to 4.5 mM and victoria blue BO from 0.1 to 0.75 mM and rhodamine B from 0.07 to 0.3 mM. The liquids were mixed for 20 min with a shaker. After the mixtures were separated for 5 min by a magnet rod, the concentrations of dyes in the supernatants were determined by spectrophotometry. The influences of pH, ionic strength (NaCl from 0 to 0.3 M), and time on the adsorption of congo red and victoria blue BO was investigated. The sorption time was carried out from 0 to 20 min. The pH of liquid was adjusted from 3.6 to 11. In all the experiments, the dye concentration in the supernatant was determined by spectrophotometry.

Adsorption of EDCs to the Fe_3O_4@C_{18}ADB@Zn_2SiO_4 material

The BPA and NP mixed aqueous solution were treated with 0.05% (w/v) of the hybrid material. The influences of pH and time on the adsorption of NP were investigated. The sorption time was carried out from 0 to 30 min. The pH was carried out from 3.6 to 11. The magnetic separation time is 5 min. The concentrations of BPA and NP in the supernatants were determined by a high-performance liquid chromatography (HPLC) with a DAD detector (Model LC 2000, Hitachi, Japan). NP was detected at 5.3 min at 278 nm, where he flow phase consisted of CH_3OH and H_2O according to 85:15 at 1.0 ml/min through a chromatographic column (Model Allsphere ODS-25 μm, Length 250 mm). BPA was detected at 4.2 min at 278 nm where the flow phase consisted of CH_3OH and H_2O according to 60:40 at 1.0 ml/min through the same column. The injection volume was 20 μl.

Photocatalysis of the resultant dye sludge

0.5% (w/v) of the Fe_3O_4@C_{18}ADB@Zn_2SiO_4 hybrid composite was added into 50 ml of 2 mM congo red. The liquid was mixed for 20 min with a shaker and then the sludge separated with a magnet rod for 10 min. The sludge was washed repeatedly with deionized water to remove the excessive dye. 0.16 g of the dye-Fe_3O_4@C_{18}ADB@Zn_2SiO_4 sludge was degraded in the photochemical reaction instrument by the addition of 3.5 ml of 30% (v/v) H_2O_2 and 0.3g of Na_2SO_4 for 70 min. The sludge was separated with a magnet rod for 5 min and washed repeatedly with deionized water to remove the excessive H_2O_2 and salt. The photos of the sludge were taken with the inverted fluorescence microscopy.

Regeneration of the sorbent

1 g of C_{18}ADB was dissolved in 20 ml of 35% (v/v) ethanol and 0.42 g of the sludge photodegraded in the presence of Na_2SO_4 added. The liquid was put into a 40 ^oC bath. After 24 h, the sludge was separated with a magnet rod for 5 min and washed repeatedly with deionized water to remove the excessive C_{18}ADB. It was used as the regenerated sorbent.

Adsorption of dyes to the regenerated sorbent

0.1 mM victoria blue BO and 0.25 mM reactive brilliant red X-3B were adsorbed with the regenerated sorbent. The liquids were mixed for 20 min with a shaker. After the liquids were separated with a magnet rod for 5 min, the dye concentration in the supernatants was determined by spectrophotometry. The above photocatalysis – regeneration and adsorption process was recycled for three times.

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Figures S1 – S6 and **Table S1**

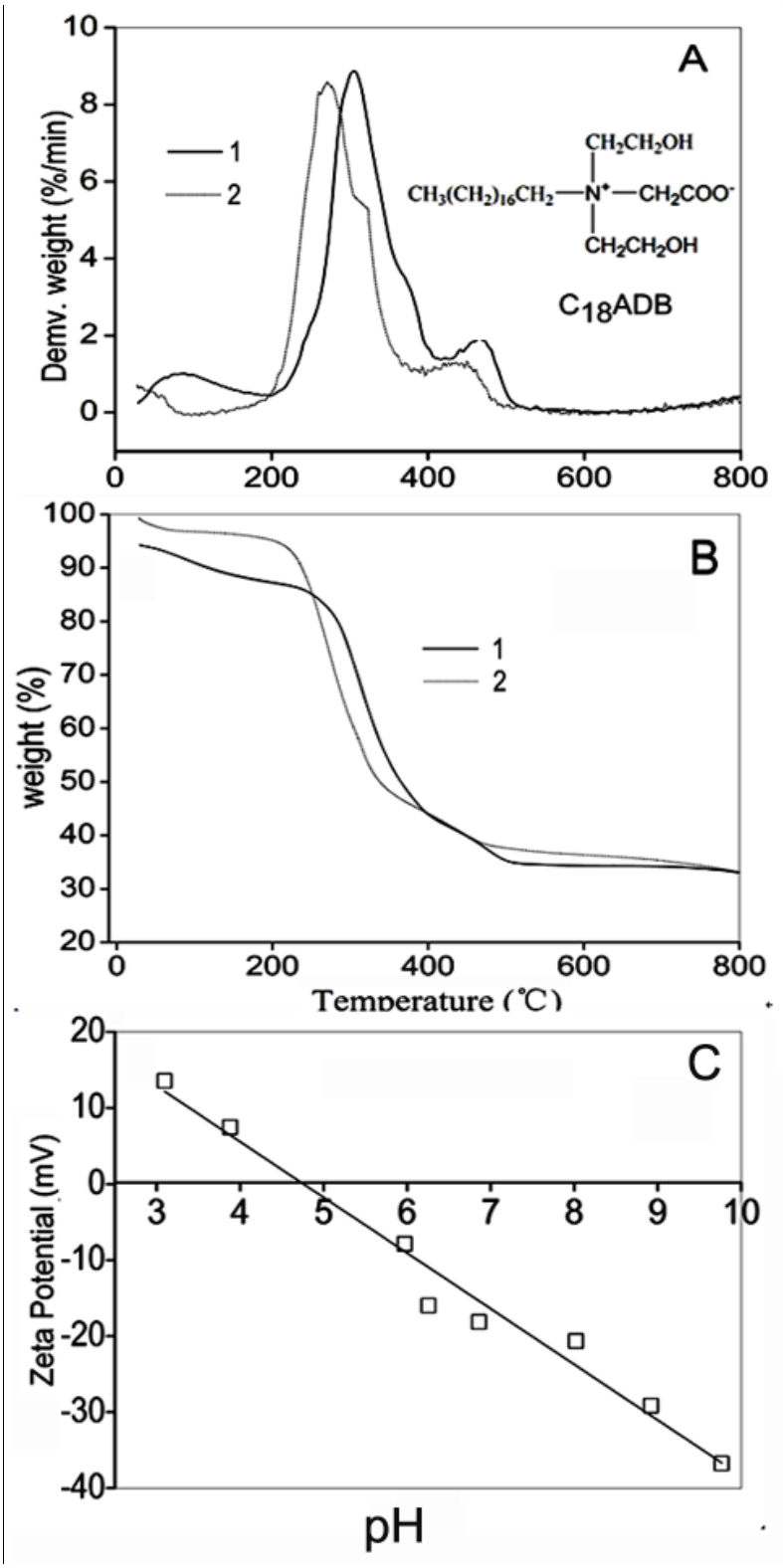

Fig. S1 A: DTA of the Fe_3O_4@C_{18}ADB@Zn_2SiO_4 (1) and Fe_3O_4&C_{18}ADB(R)@Zn_2SiO_4 (2) material. **B:** TGA of the Fe_3O_4@C_{18}ADB@Zn_2SiO_4 (1) and Fe_3O_4&C_{18}ADB(R)@Zn_2SiO_4 (2) material. **C:** ζ-potential change of the Fe_3O_4@C_{18}ADB@Zn_2SiO_4 hybrid composite

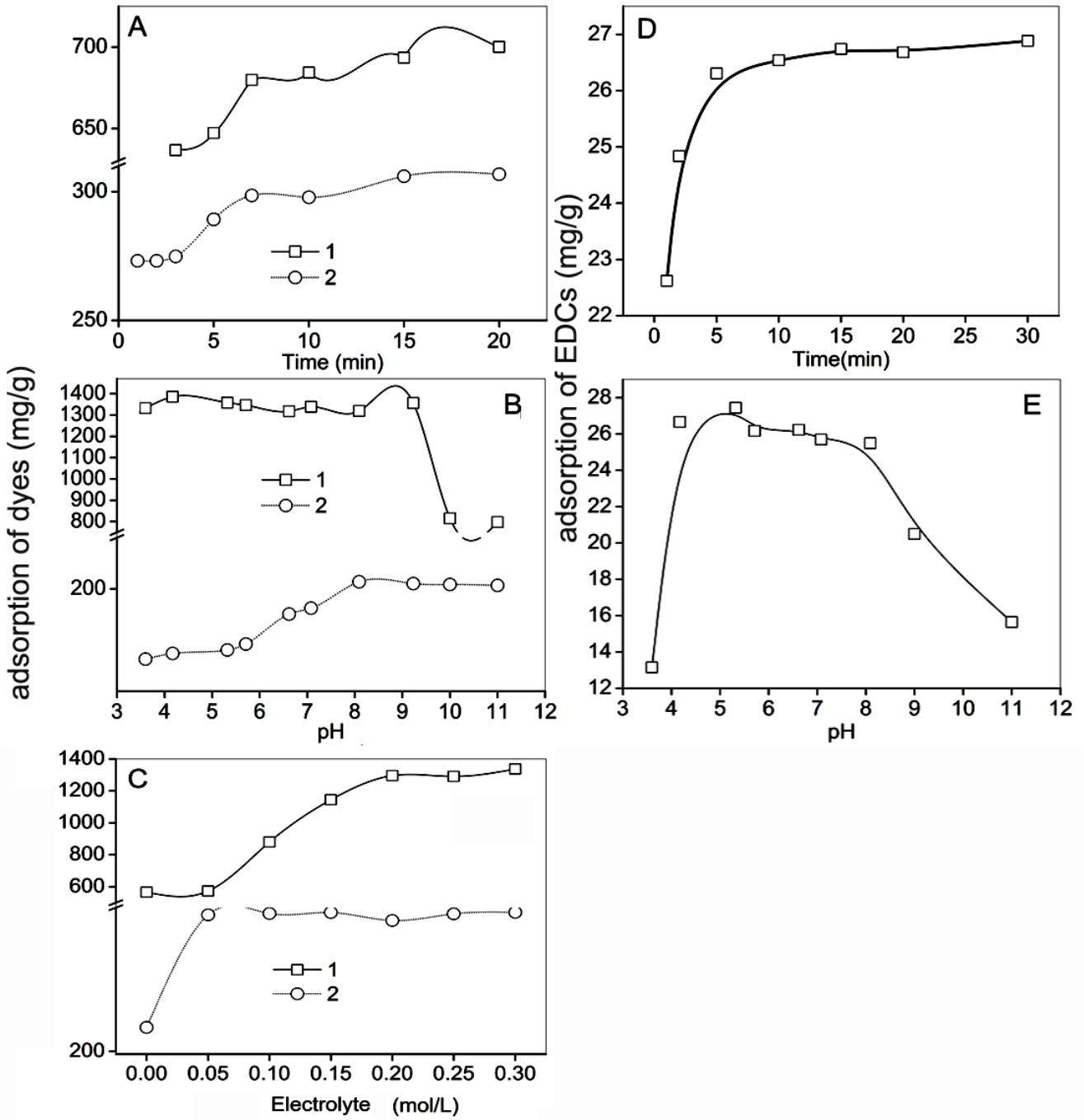

Fig. S2 A: the sorption curve of dyes (1- congo red, 2-victoria blue BO) to the Fe_3O_4@C_{18}ADB@Zn_2SiO_4 material at different times. **B**: the sorption curve of dyes (1- congo red, 2-Victoria pure blue BO) at different pH. **C**: effect of ionic strength on the adsorption of dyes (1- congo red, 2-victoria blue BO). **D**: Effect of time on the adsorption of NP. **E**: Effect of pH on the adsorption of NP.

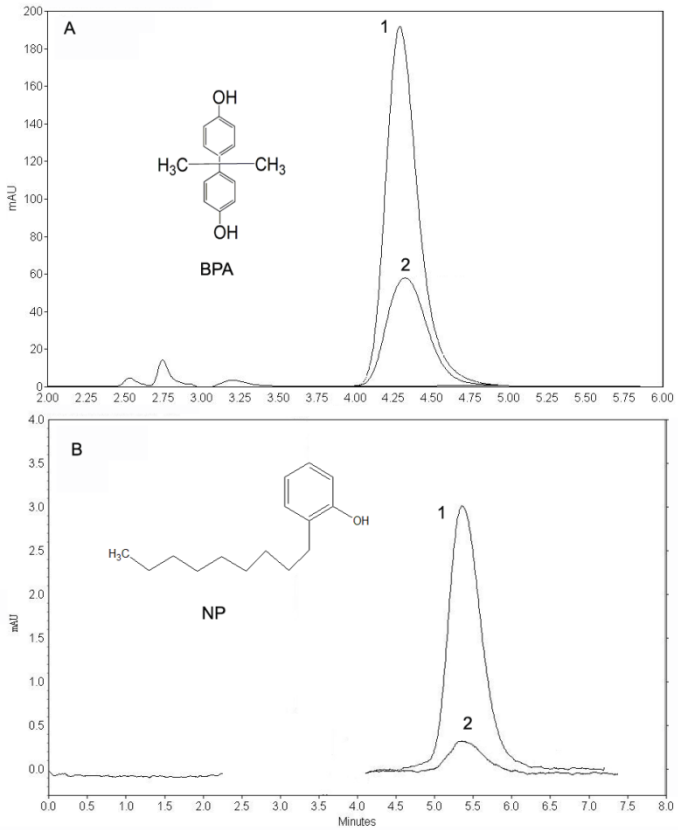

Fig. S3 HPLC chromatograph of the solution containing 1.0 mg/L BPA (A1) and 5.5 mg/L NP (B1) and its supernatant (A2 and B2) after it was treated with the Fe_3O_4@C_{18}ADB@Zn_2SiO_4 hybrid composite (0.05% (w/v)).

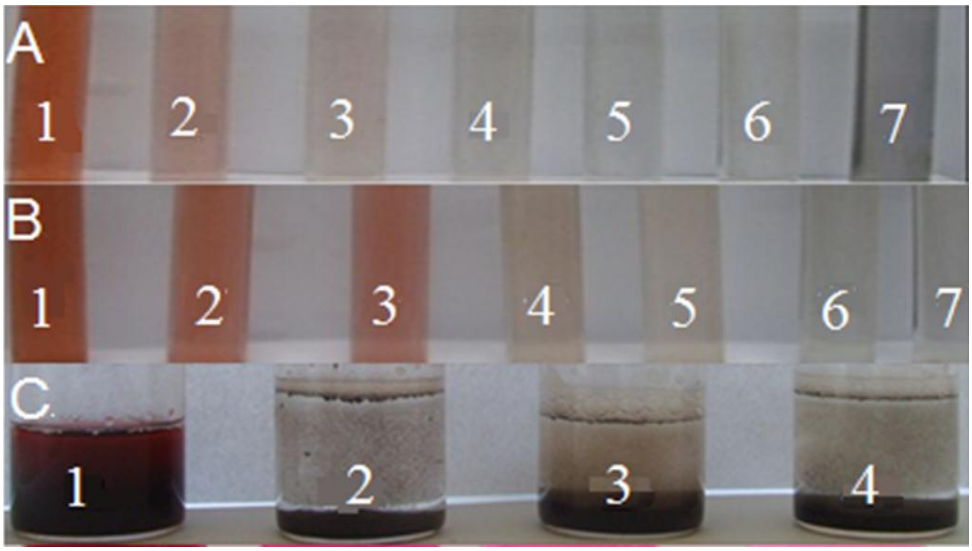

Fig. S4 A: the dye-Fe_3O_4@C_{18}ADB@Zn_2SiO_4 sludge (0.16 g) liquid was degraded for 70 min in the presence of 0 (A2), 2.5 (A3), 3 (A4), 3.5 (A5) and 4 ml (A6) of H_2O_2 in UV light, A1: the dye solution without photocatalysis, A7: the Fe_3O_4@C_{18}ADB@Zn_2SiO_4 hybrid composite -only liquid. **B:** the same as A5 but at 0 (B1), 5 (B2), 15 (B3), 30 (B4), 50 (B5), 70 (B6) and 90 min (B7). A and B are the photocatalytic solutions diluted for ten times with deionized water. **C**1: the dye-Fe_3O_4@C_{18}ADB@Zn_2SiO_4 sludge (0.16 g) liquid, C2 the same as C1 but degraded for 70 min in the presence of 3.5 ml of H_2O_2 in UV light, C3: the same as C2 but with 0.3 g of Na_2SO_4 and C4 with 0.3 g of NaCl.

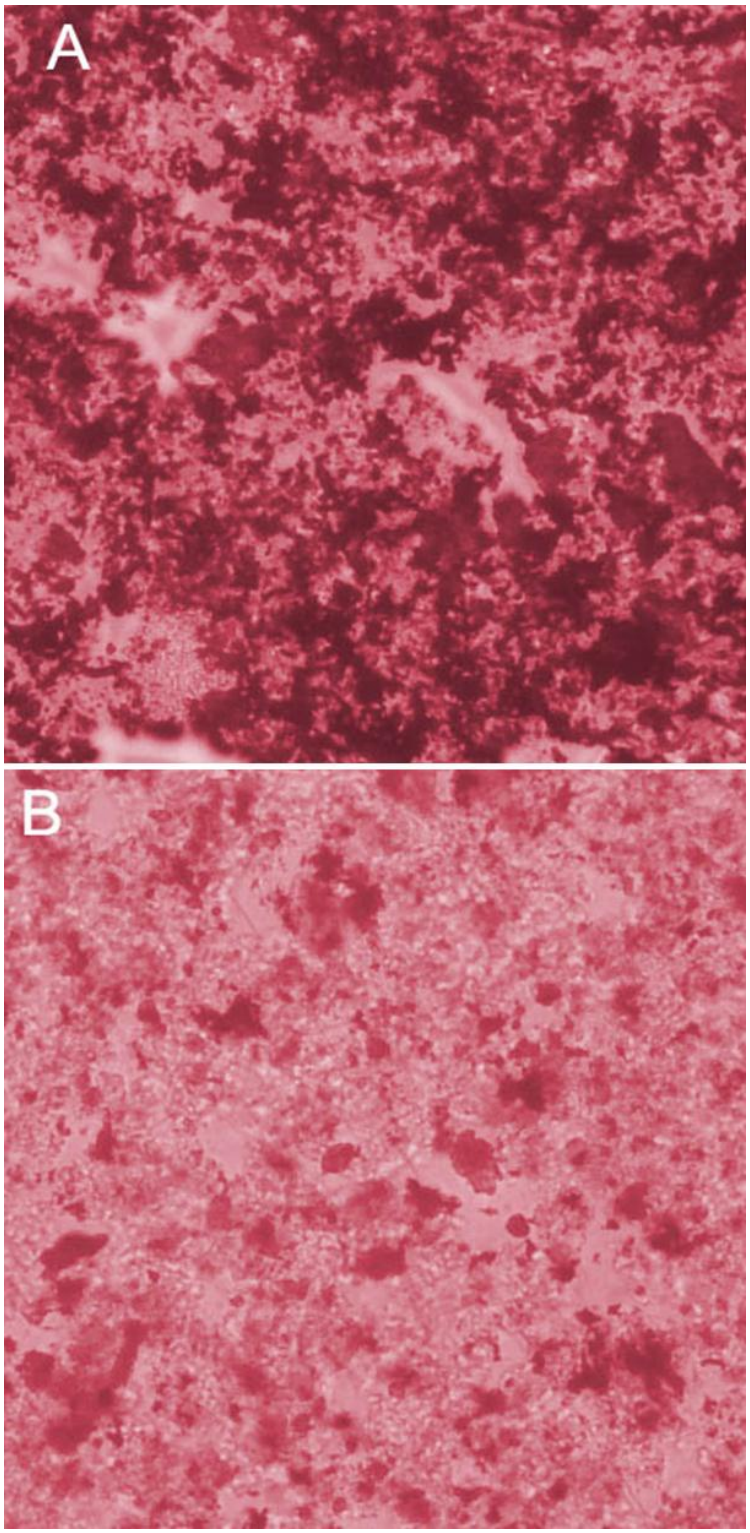

Fig. S5 Microscopic images of the dye-Fe_3O_4@C_{18}ADB@Zn_2SiO_4 sludge degraded for 70 min (A) by UV/H_2O_2 photocatalysis and the same one but in the presence of Na_2SO_4 (B)

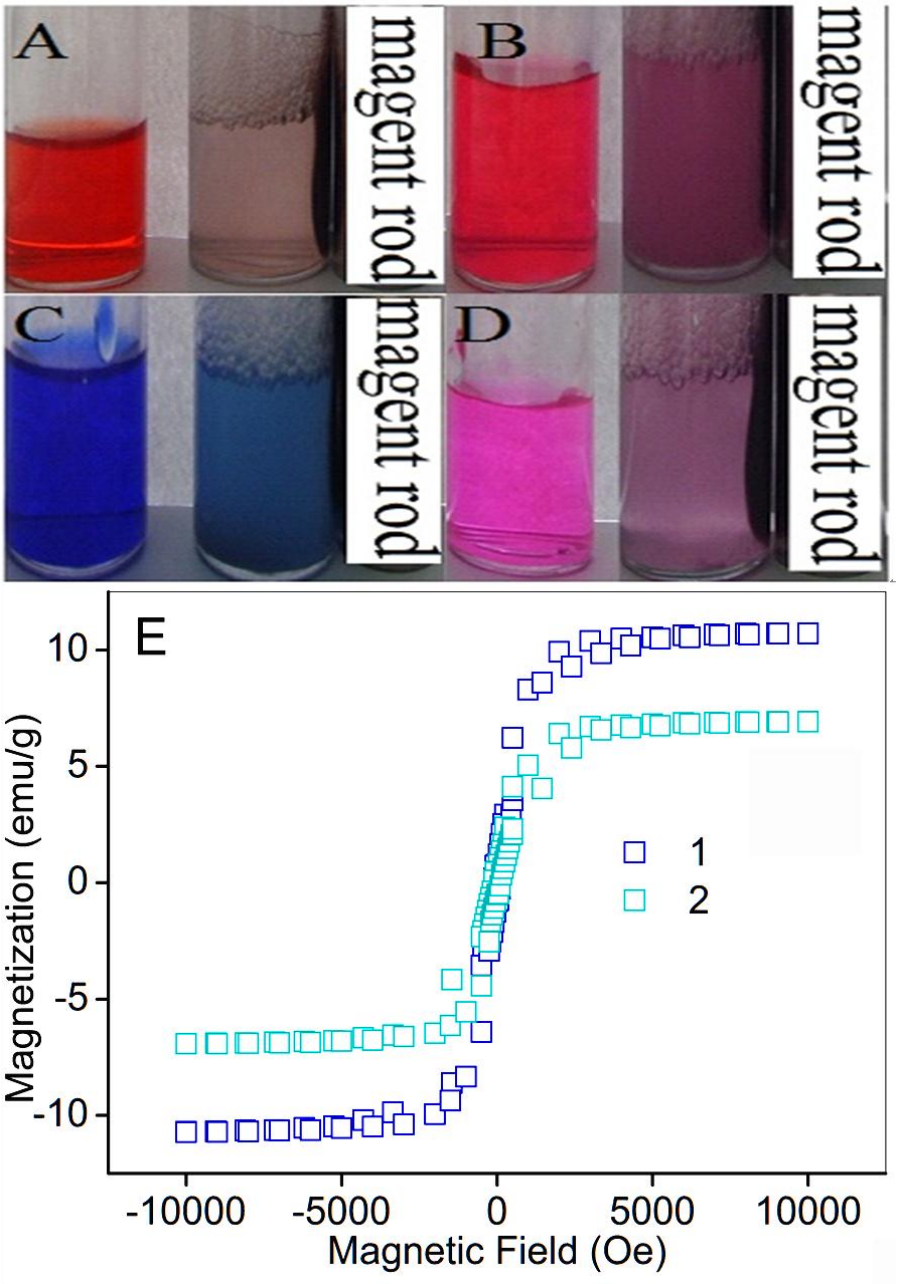

Fig. S6 Photos of 0.1 mM congo red (A1), 0.1 mM reactive brilliant red X-3B (B1), 0.02 mM victoria blue BO (C1) and 0.01 mM rhodamine B (D1) and their adsorption and magnetic separation (A2-D2) with 0.1% (w/v) the Fe_3O_4@C_{18}ADB@Zn_2SiO_4 hybrid composite. The hysteresis curves for the freshly prepared Fe_3O_4@C_{18}ADB@Zn_2SiO_4 hybrid composite (E1) and the regenerated sorbent (E2).

Table S1 Change of C and N contents in the dye-Fe_3O_4@C_{18}ADB@Zn_2SiO_4 sludge degrading by UV/H_2O_2 photocatalysis in the presence of Na_2SO_4.

photocatalytic degradation time, min	C %	N %	C/N
0	37.2	3.6	10.3
5	35.7	3.5	10.2
15	36.6	3.6	10.3
30	32.4	3	10.8
50	27.1	2.4	11.3
70	26.6	2.3	11.1
90	26.8	2.3	11.6
150	25.0	2.1	11.9