

## **Electronic Supplementary Information (ESI)**

### **SDBS@BaSO<sub>4</sub>: an efficient wastewater-sorbing material**

#### **SI text**

##### **Apparatus and materials**

A photodiode array spectrometer (Model S4100, Scinco, Korea) with the Labpro plus software (Firmware Version 060105) was used to determine chromaticity and concentration of various color compounds and suspending substance liquids. A particle size analyzer (Model LS230, Beckman Coulter, USA) with a Laser Channel (Model LFC-101, Ankersmid, Holland) was used to measure the size distribution and specific surface area (SSA) of the material particles. The thermal gravity analysis (TGA) of the material powder was carried out with a thermogravimetry (Model TAQ 600, USA). An X-ray diffractometer (XRD) (Model D/max2550VB3+/PC, Rigaku, Japan) was used for identifying the structure and size of crystal particles. A scanning electronic microscopy (SEM) (Model Quanta 200 FEG, FEI Co., USA) was used to measure the size and shape of the materials. A high resolution transmission electronic microscopy (TEM) (Model Tecnai G2 F20 S-Twin, FEI Co., USA) (120 kV, 2.4 Å resolution) was used to measure the distribution of BaSO<sub>4</sub> and SDBS in the particle fragments. A surface area analyzer (Model TriStar 3000, Micromeritics Co., USA) with N<sub>2</sub> as adsorptive was used to measure the specific surface area of materials. An X-ray fluorescence (XRF) (Model SRS3400, Bruker, Germany) was used to determine the Ba and S contents in the material. A high-frequency infrared radiation carbon - sulfur analyzer (Model HW2000, Wuxi Yingzhicheng High Speed Analyzing Apparatus Instrument Co., China) was used to determine carbon and sulfur elements contents in the powder materials. A spectrofluorometer (Mode F-4500, Hitachi, Japan) was used to determine the POPs concentration in each independent POP solution. A high performance liquid chromatography (HPLC) (Model L-2000, Hitachi, Japan) was used to determine the POPs in the POPs-dye mixed solution and chlorobenzene compounds in chemical wastewater, which were performed with a L-2130 pump, diode array detector (DAD) (Model L-2455) and an inversed-phase column (Model Allsphere ODS-2, 5 μm, 250 mm × 4.6 mm). A ζ-potential analyzer (Model Z-2000, Malvern, England) was used to determine the surface potential of the material particles. A programable digestion system (Model 5B-1, Lanzhou, China) and a portable water quality rapid analyzer

(Model PORS-15V, Pgeneral Co., China) with the COD calculation software were combined to determine COD of dye wastewaters.

Sodium dodecyl benzene sulfonate (SDBS) (purity 83%) was purchased from ShangHai Reagent Company (SRC, China) and 5 mM was prepared by dissolving 1.7424 g of SDBS in 1000 mL deionized water. A SDBS standard solution (500 mg/L) (Institute for Reference Materials of SEPA of Beijing, China) was to used for correction of the SDBS reagent purity. 10 mM barium chloride and 10 mM sodium sulfate (SRC) were prepared. 2 mM basic violet 6B (BV), 2 mM methylene blue (MB), 1 mM weak acidic green GS, 2 mM reactive brilliant red X-3B, 1 mM safranin T (ST) and 1 mM cetylpyridinium chloride monohydrate (CPC) (all from SRC, China) were prepared in deionized water. Phenanthrene (Phe) (purity 97%), fluorene (Flu) (purity 99%), biphenyl (Bip) (purity 97%) and naphthalene (Nap) (purity 99.8%) (all from Fluka Chemical Co.) were prepared in deionized water, all in 2 mg/L. Granular activated carbon (800-1000 m<sup>2</sup>/g SSA, Shanghai Experiment Reagent Co.) was used to compare the adsorption property with the inclusion material. Acetonitrile (purity>99.8%, Mallinckrodt Baker, Inc.) was used as the flow liquid of HPLC. A chlorobenzenes standard solution containing 1, 2-dichlorobenzene 201.9 µg/mL, 1, 3-dichlorobenzene 204.8 µg/mL, 1, 4-dichlorobenzene 201.5 µg/mL and 1, 2, 4-trichlorobenzene 102.0 µg/mL (Institute for Reference Materials of SEPA, Beijing, China) was used to prepare a chemical sewage mixed with urban sewage. Two wastewaters were sampled from two cationic dye plants, one of which is from Jinjiang dye-producing plant (Hangzhou, China) with 220000 of colority and 6500 mg/L COD and the other from Xingwu dye-producing plant (Nantong, China) with 4300 of colority and 3700 mg/L COD.

## Methods

**Synthesis of the material.** SDBS (10 g) and 20 g sodium sulfate were dissolved in 2000 ml deionized water. Barium chloride (500 ml of 20%) was added slowly with stirring. After 10 min, the liquid was incubated for about 30 min to precipitate the suspended substances. The precipitate was washed three times with 3000 ml deionized water. The final suspension with the BaSO<sub>4</sub>-SDBS hybrid material was used for further experiments. Some of it was aged for 4 h and centrifuged at 5000 rpm for 5 min and the pellet was dried at 110°C to prepare the material powder. The solid content of the liquid material was determined and the powder was used to analyze the particle size, pattern and structure. Using the same method, the BaSO<sub>4</sub>-SDBS surface-modified material was prepared following the sequence: SO<sub>4</sub><sup>2-</sup> - Ba<sup>2+</sup> - SDBS, and the suspension was prepared in the

absence of SDBS. The difference in adsorption performance between the BaSO<sub>4</sub>-only and the hybrid material was assessed.

**Composition determination and structural characterization:** To dissolve 12.6 mg of the hybrid material powder, 50 ml of EDTA (0.16 M) in 10% aqueous ammonia was added. The Ba and S contents of the material powder were determined by XRF and their molar ratio was calculated. The amount of SDBS was determined by the difference in light absorption (see spectrophotometry, below). The composition ratio of the material, i.e. Ba<sup>2+</sup>:SO<sub>4</sub><sup>2-</sup>:SDBS, was calculated. TGA, XRD, TEM and SEM were performed on the powdered materials and their ζ-potentials and particle size distributions were examined in the SS liquids.

**Adsorption of dyes and POPs.** Four dye solutions were prepared to examine the adsorption selectivity of the materials: two anionic dyes, weak acidic green GS and reactive brilliant red X-3B; and two cationic dyes, BV and MB. Each was treated with 0.02% BaSO<sub>4</sub>-only, BaSO<sub>4</sub>-SDBS surface-modified and BaSO<sub>4</sub>-SDBS hybrid materials. The color change of the dyes after treatment with hybrid material was compared with that of the corresponding dye solution with no adsorbent. The cationic dyes BV and MB were selected to investigate the mechanism of adsorption by the material. To a series of 10-ml MB solutions ranging from 0 to 0.2 mM, a known volume of the hybrid material liquid was added. After mixing for 10 min, the liquids were incubated for 30 min and the concentration of MB in each supernatant was determined by spectrophotometry, in the presence of CPC to mask interference by leached SDBS. Using the same method, the adsorption of 0 to 1.2 mM BV was determined. The molar amounts of BV and MB bound to the material were calculated. Activated carbon was also used as a conventional sorbent and compared with the hybrid material. The effects of pH from 0.05 to 9.29 on the adsorption of MB and from 0.96 to 9.46 on the adsorption of BV, of ionic strength between 0 and 1 M and of temperature between 10 and 50°C were examined. The Langmuir isothermal adsorption equation was used to fit the association of MB and BV with the hybrid material, where *K* is an empirical constant and *N* is the maximum molar amount of dye bound. To 0.20 mg/l aqueous solutions of Phe, Flu, Bip and Nap, 0.03% of the BaSO<sub>4</sub>-only, BaSO<sub>4</sub>-SDBS surface-modified and BaSO<sub>4</sub>-SDBS hybrid materials were added. After mixing for 10 min, all the mixtures were incubated for 30 min. Each supernatant was evaluated by spectrofluorometry. The rates of removal of the POPs were calculated and compared. To a series of POP standard solutions - Phe from 0 to 1.10 mg/l, Flu from 0 to 0.40 mg/l, Bip from 0 to 1.10 mg/l and Nap from 0 to 0.50 mg/l - 0.03% of

the hybrid material was added and the POP concentrations in the supernatants were determined. The amounts of POP captured in the hybrid sorbent were calculated and  $K_{pw}$  values were obtained. Thus, the relationship between  $K_{ow}$  and  $K_{pw}$  was established for each POP. Different adsorption mechanisms may be involved in the removal of POPs and cationic dyes by the hybrid material. A solution containing 1 mg/l Phe and 1 mM BV was prepared to study mutual interference in adsorption by the hybrid material. In a series of such solutions, Phe ranged from 0 to 0.45 mg/l with BV from 0 to 0.45 mM, and 0.03% of the hybrid material was added in each case. The concentrations of BV and Phe in each supernatant were determined by spectrophotometry and HPLC and the amounts captured by the hybrid material were calculated.

**Application to treatment of wastewater.** The BaSO<sub>4</sub>-SDBS hybrid material was added over the concentration range 1-3% to the first dye wastewater, 0.2-1% to the second and at 0.01, 0.05 and 0.10% to the chemical sewage. After mixing for 5 min and incubation for 30 min, the colors of the dye wastewater supernatants were determined by spectrophotometry and the COD was measured with a rapid COD analyzer. The free POP concentration in the chemical sewage supernatant was determined by HPLC. The removal of the color, the COD and the chlorobenzene concentration were calculated.

### Instrumentations

**SDBS.** In the composition determination of the inclusion material, SDBS dissolved in the EDTA-NH<sub>3</sub>-H<sub>2</sub>O solution was determined according to the following procedures (Gao H. W.; Ye Q. S.; Liu W. G., *Anal. Sci.* **2002**, *18*, 455.). Into a solution, 0.5 mL of 1 mM ST and 0.2 mL of pH 11 phosphate buffer solution were added. The solution was diluted to 10 ml and mixed well. After reacting for 10 min, the absorbances ( $A_{600nm}$  and  $A_{500nm}$ ) of the solution were measured at  $A_{600nm}$  and  $A_{500nm}$  against water. The absorbance ratio difference

( $\Delta A_r$ ) was calculated by  $\Delta A_r = \frac{A_{600nm}}{A_{500nm}} - \frac{A_{600nm}^0}{A_{500nm}^0}$ , where  $A_{600nm}^0$  and  $A_{500nm}^0$  are the absorbances of a reagent

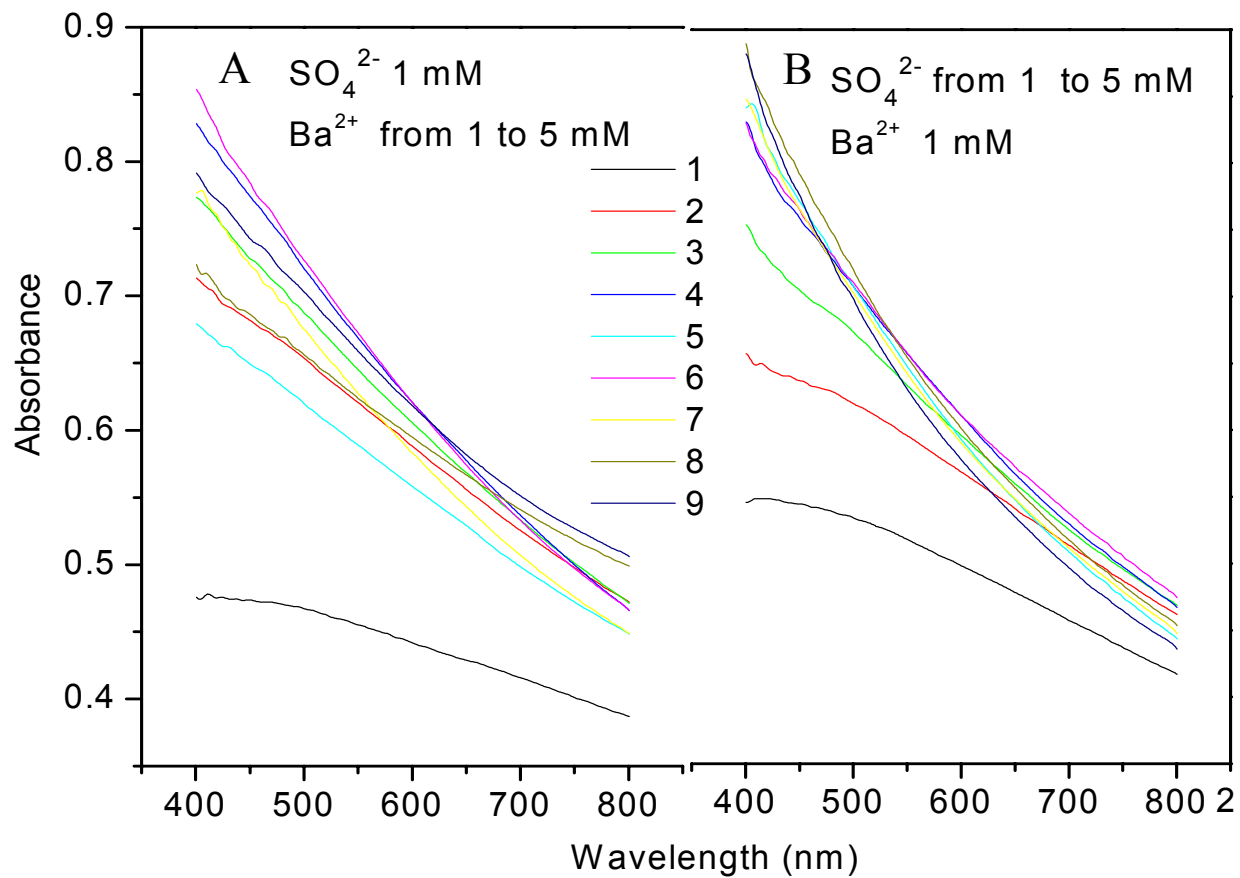
blank without SDBS against water. Finally, the SDBS concentration was calculated from plots  $\Delta A_r$  vs.  $c_{SDBS,0}$  (Fig. S4 B). The SDBS concentration stayed in supernatants during evolution of the reaction rate in synthesis of the inclusion material and determination of leaching rate of the product powder was determined at 223 nm directly by UV spectrophotometry.

**POPs.** The supernatant of an independent POP solution was measured directly by spectrofluorometry at  $\lambda_{\text{ex}}$  247 nm and  $\lambda_{\text{em}}$  367 nm for Phe,  $\lambda_{\text{ex}}$  262 nm and  $\lambda_{\text{em}}$  310 nm for Flu,  $\lambda_{\text{ex}}$  248 nm and  $\lambda_{\text{em}}$  312 nm for Bip and  $\lambda_{\text{ex}}$  275 nm and  $\lambda_{\text{em}}$  330 nm for Nap. In the Phe-BV mixed-solutions, BV was determined directly at 550 nm by spectrophotometry but Phe at 280 nm by HPLC with DAD, where the flow rate of the elution mixing water (25%) with acetonitrile (75%) is at 1.0 mL/min.

**Chlorobenzene compounds.** Their concentrations were determined at 210 nm by HPLC. The gradient elution was carried out from 55% deionized water and 45% acetonitrile at the beginning to 15% and 85% at 15 min, and then to 10% and 90% at 18 min. 20  $\mu\text{l}$  of a supernatant was injected and the flow rate of the mixed mobile phase 1.0 ml/min.

**COD.** At first, an oxidant solution was prepared by dissolving 40 g of mercuric sulfate and 24.516 g of potassium dichromate in 800 mL of deionized water and 70 mL of concentrated sulphuric acid was added slowly. The solution was diluted to 1000 mL with deionized water and fixed well. A catalyst solution was prepared by dissolving 25 g of solver sulfate in 500 mL of concentrated sulphuric acid, too. 2.0 mL of a dye wastewater were added into the clean glass tube. 1.0 mL of the oxidant solution and 3.0 mL of the catalyst solution were added. The solution was digested in a programable digestion system for 30 min at 165 °C. Then 2.0 mL of deionized water was injected into the solution. The solution was cooled in water. The COD value of the wastewater sample was determined with a portable water quality rapid analyzer.

Figures S1-S13



**Fig. S1** A and B: Absorption spectra of the suspending BaSO<sub>4</sub> liquids, where Ba<sup>2+</sup> from 1.0 to 5.0 mM (from curve 1 to 9) in 0.50 mM of step were added 1.0 mM SO<sub>4</sub><sup>2-</sup> (A) and SO<sub>4</sub><sup>2-</sup> from 1.0 to 5.0 mM (from curve 1 to 9) in 0.50 mM of step were added 1.0 mM Ba<sup>2+</sup> (B).

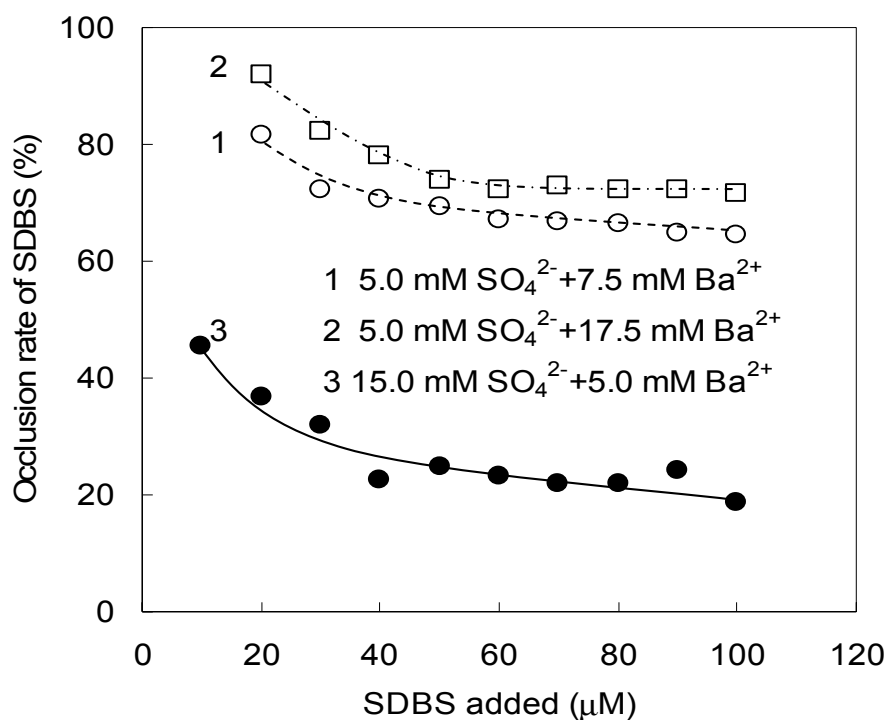


Fig. S2 Effect of mole ratio of  $\text{SO}_4^{2-}$  to  $\text{Ba}^{2+}$  on occlusion of SDBS

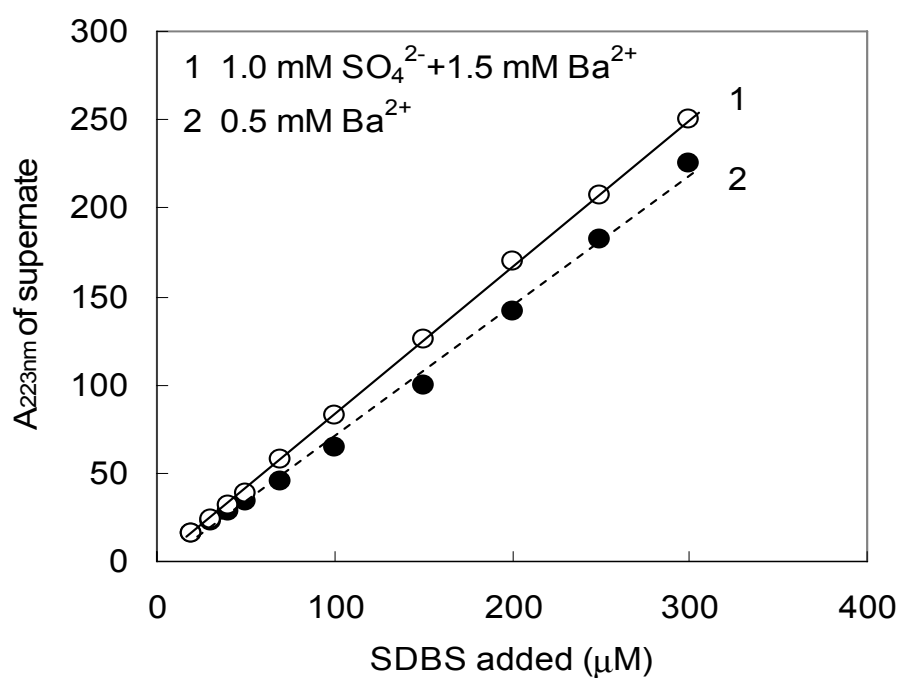
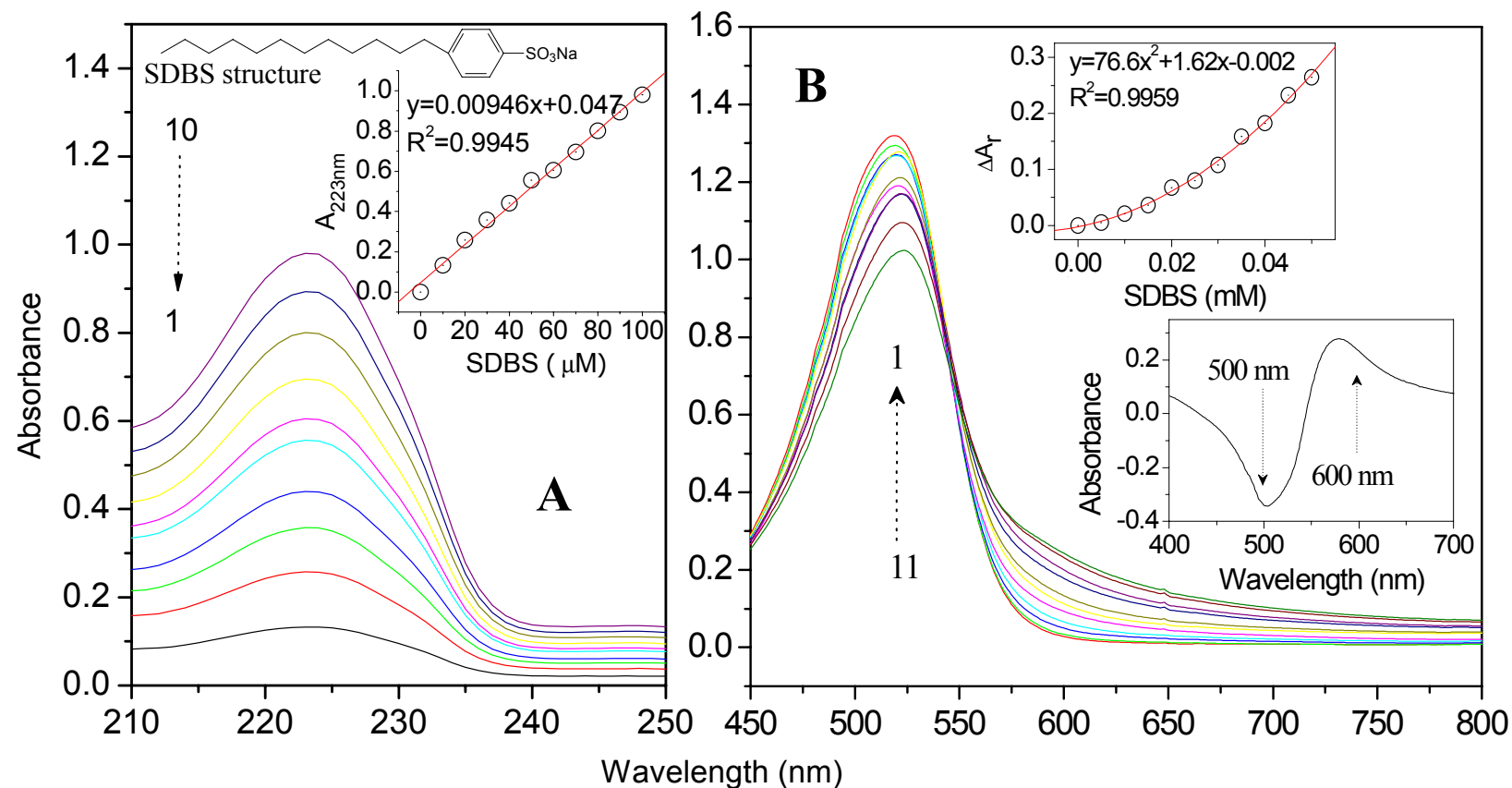
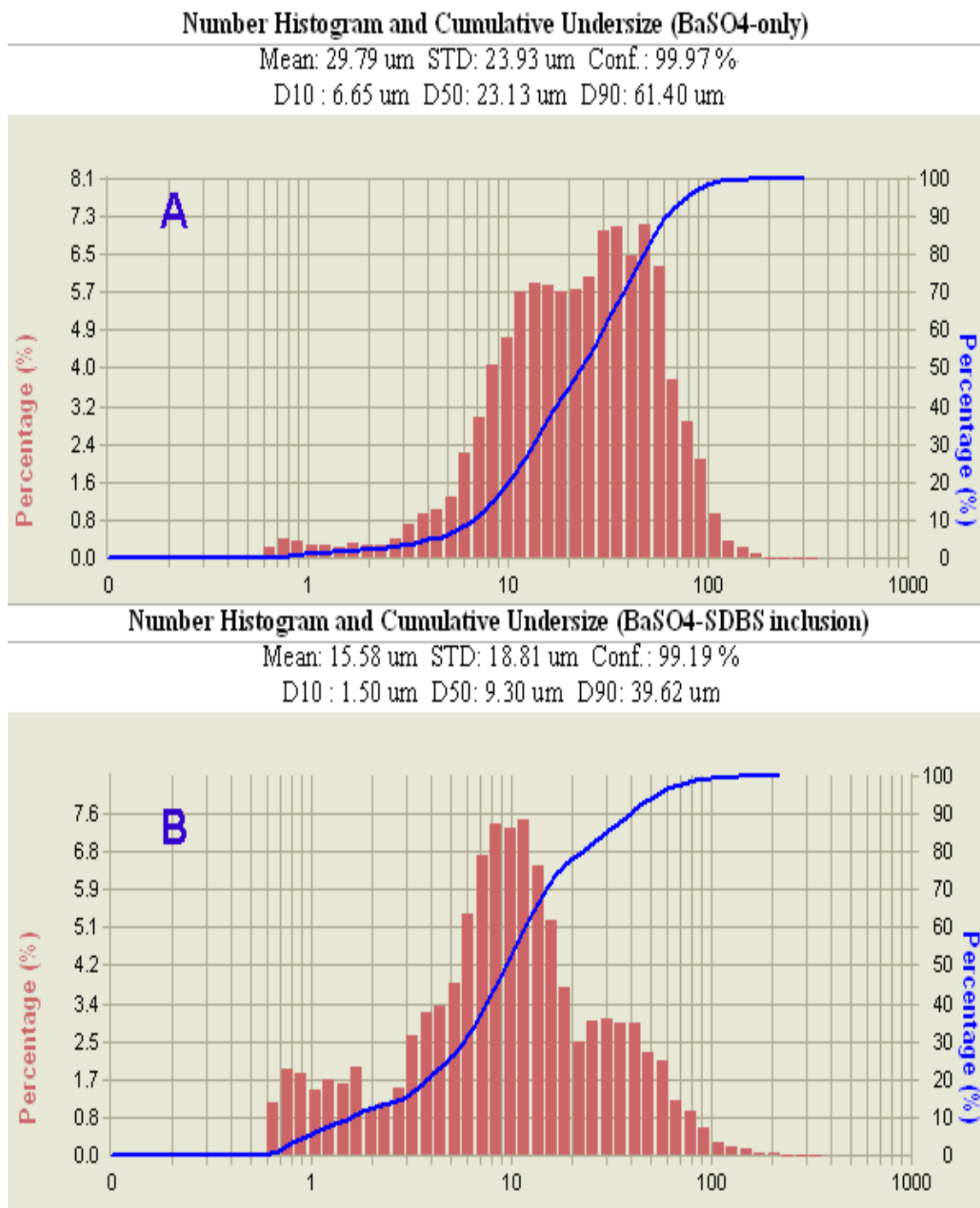


Fig. S3 Determination of SDBS in supernatants. All the SDBS liquids were centrifuged at 8000 rpm for 10 min to obtain the supernatants, 1: both 1.00 mM  $\text{SO}_4^{2-}$  and 1.50 mM  $\text{Ba}^{2+}$  were added, where 0.50 mM  $\text{Ba}^{2+}$  is excessive and 2: only 0.50 mM  $\text{Ba}^{2+}$  added.

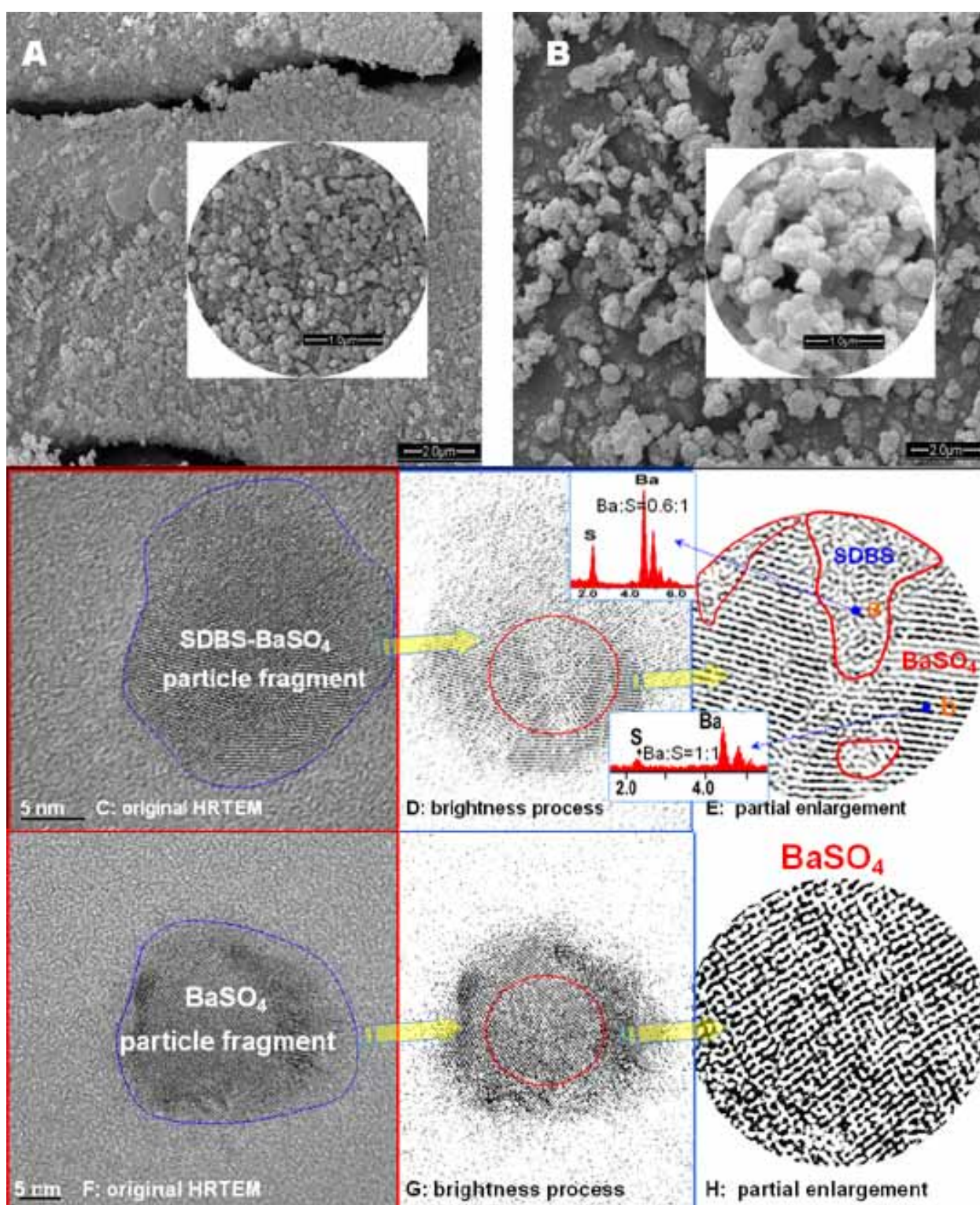


**Fig. S4** Absorption spectra and standard curves for determination of SDBS. A: SDBS between 0 and 0.10 mM (curves 1 to 10). B: SDBS between 0 and 0.05 mM (curves 1 to 11) at pH 11 with safranin T and CPC as chromagenic agents.  $\Delta A_r = A_{600\text{nm}}/A_{500\text{nm}} - A_{600\text{nm}}^0/A_{500\text{nm}}^0$  from the LARVA method, where  $A_{600\text{nm}}$  and  $A_{500\text{nm}}$  are the absorbances of spectra 2-11 at 600 and 500 nm and  $A_{600\text{nm}}^0$  and  $A_{500\text{nm}}^0$  those of spectrum 1.





**Fig. S5** Particle distribution of the object suspended adsorbent liquids. A: BaSO<sub>4</sub>-only and B: BaSO<sub>4</sub>-SDBS hybrid.



**Fig. S6** SEM (A-B) and TEM (C-H) images of BaSO<sub>4</sub>-only (A, F-H) and BaSO<sub>4</sub>-SDBS inclusion (B-E) materials. Both **a** and **b** are the measurement points for the EDX analysis of S and Ba elements.

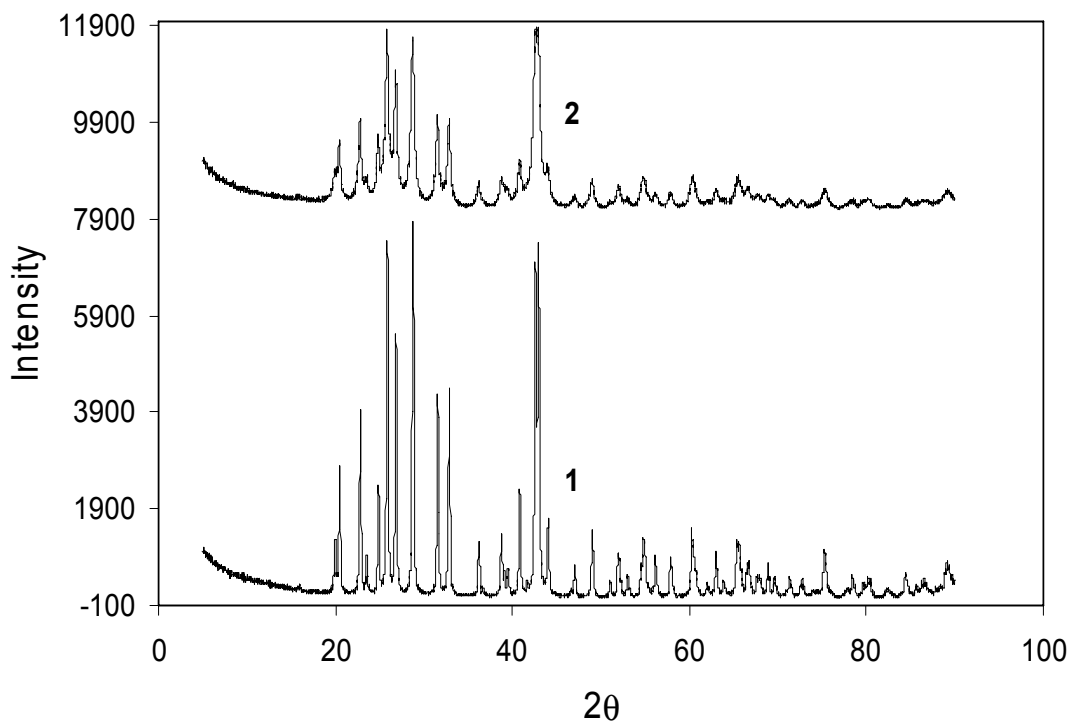


Fig. S7 XRD of BaSO<sub>4</sub>-only (1) and BaSO<sub>4</sub>-SDBS inclusion (2) materials

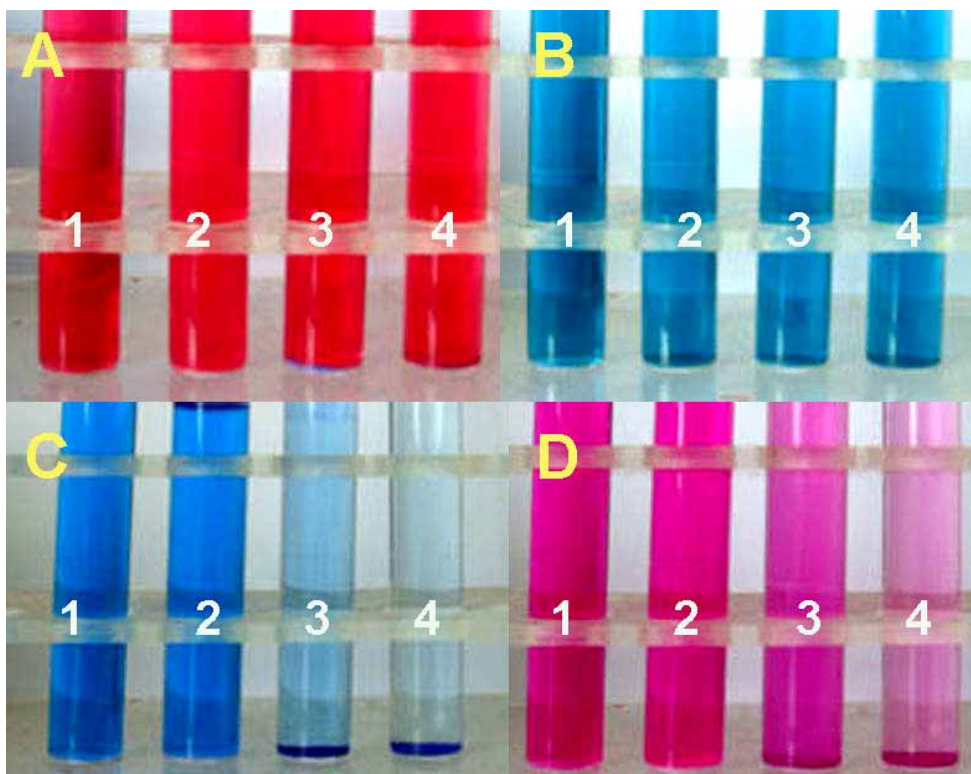
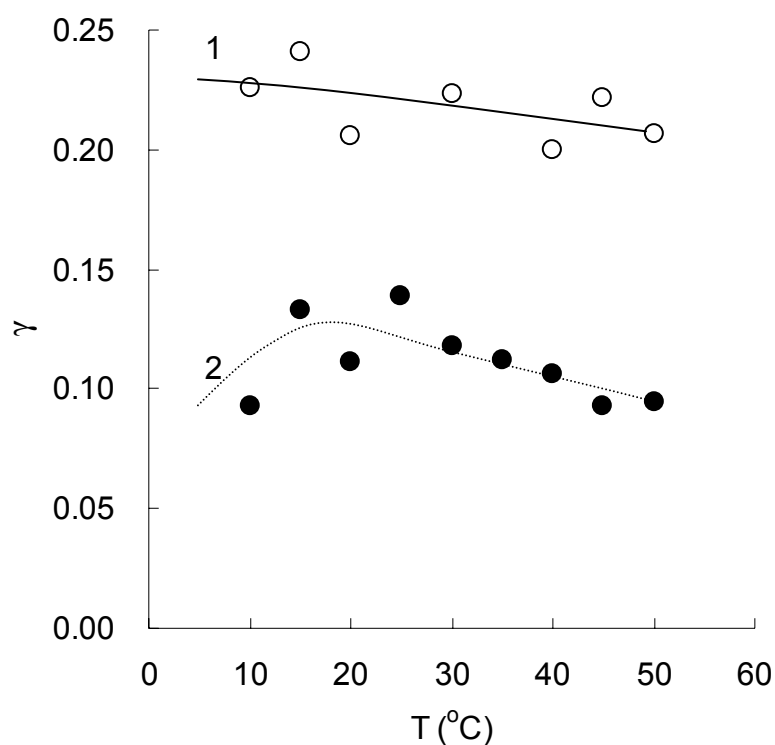
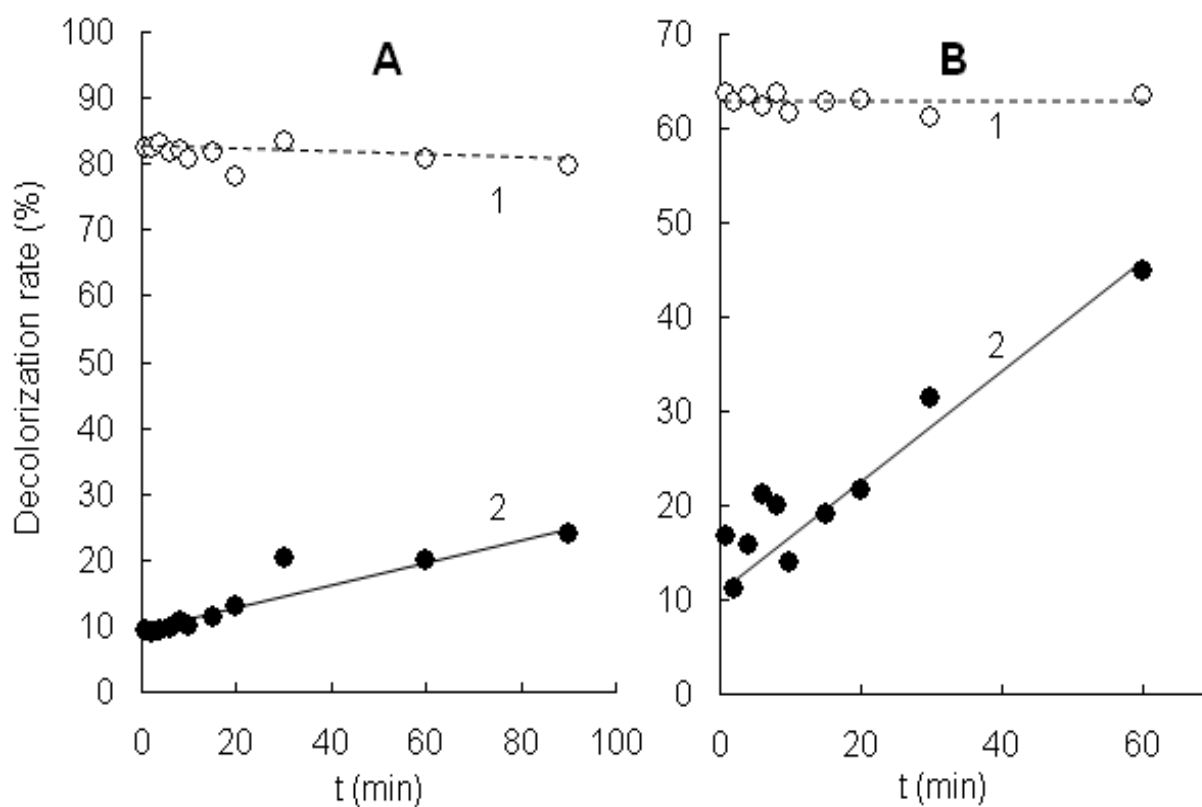


Fig. S8 Colority change of 0.01 mM reactive brilliant red X-3B (A), 0.02 mM weak acid green GS (B), 0.03 mM MB (C) and 0.03 mM BV (D) solutions, where dye-only reference (1), 0.02% BaSO<sub>4</sub>-only (2),

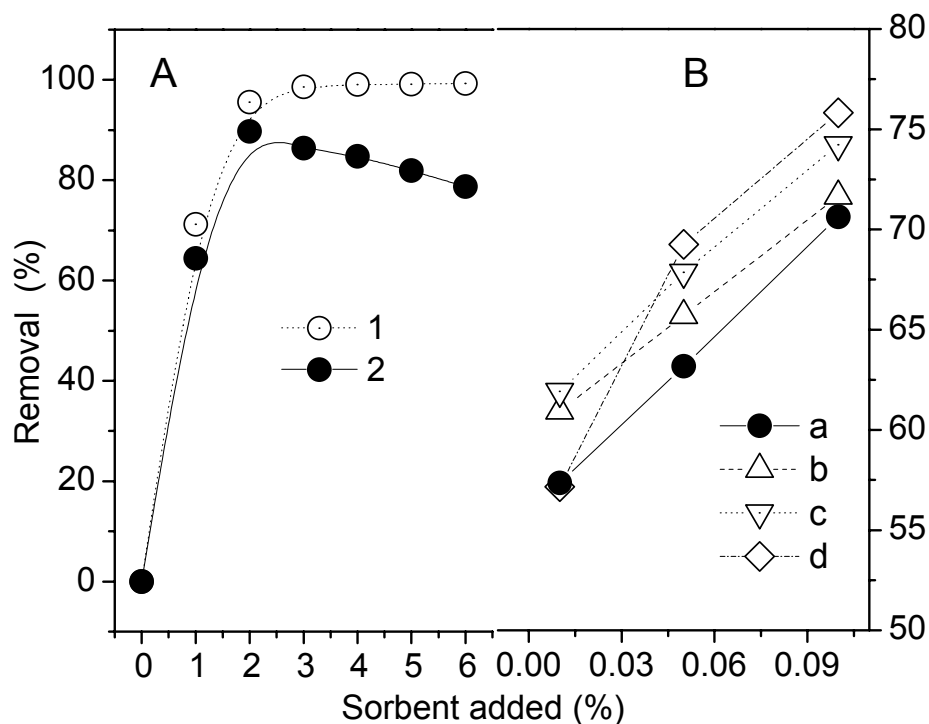
0.02% of the BaSO<sub>4</sub>-SDBS surface-modifying material (3) and 0.02% of the BaSO<sub>4</sub>-SDBS inclusion adsorbent (4) were added, respectively.



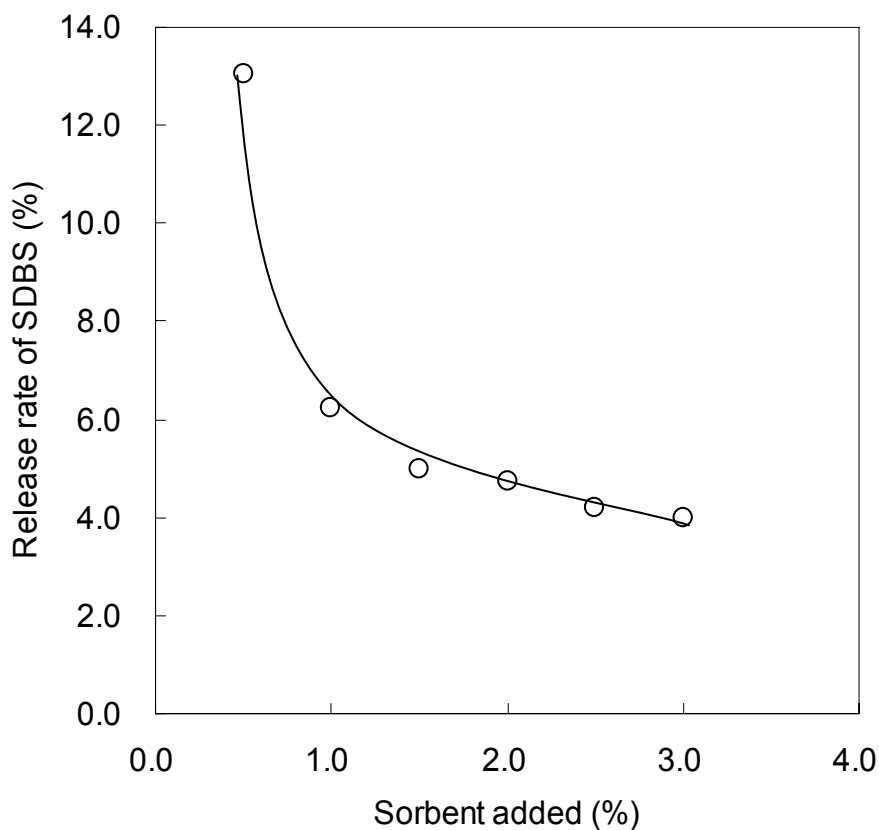
**Fig. S9** Effect of temperature on  $\gamma$  of MB and BV. 1- 0.040 mM MB and 0.020% hybrid adsorbent and 2- 0.030 mM BV and 0.030% hybrid adsorbent were added.



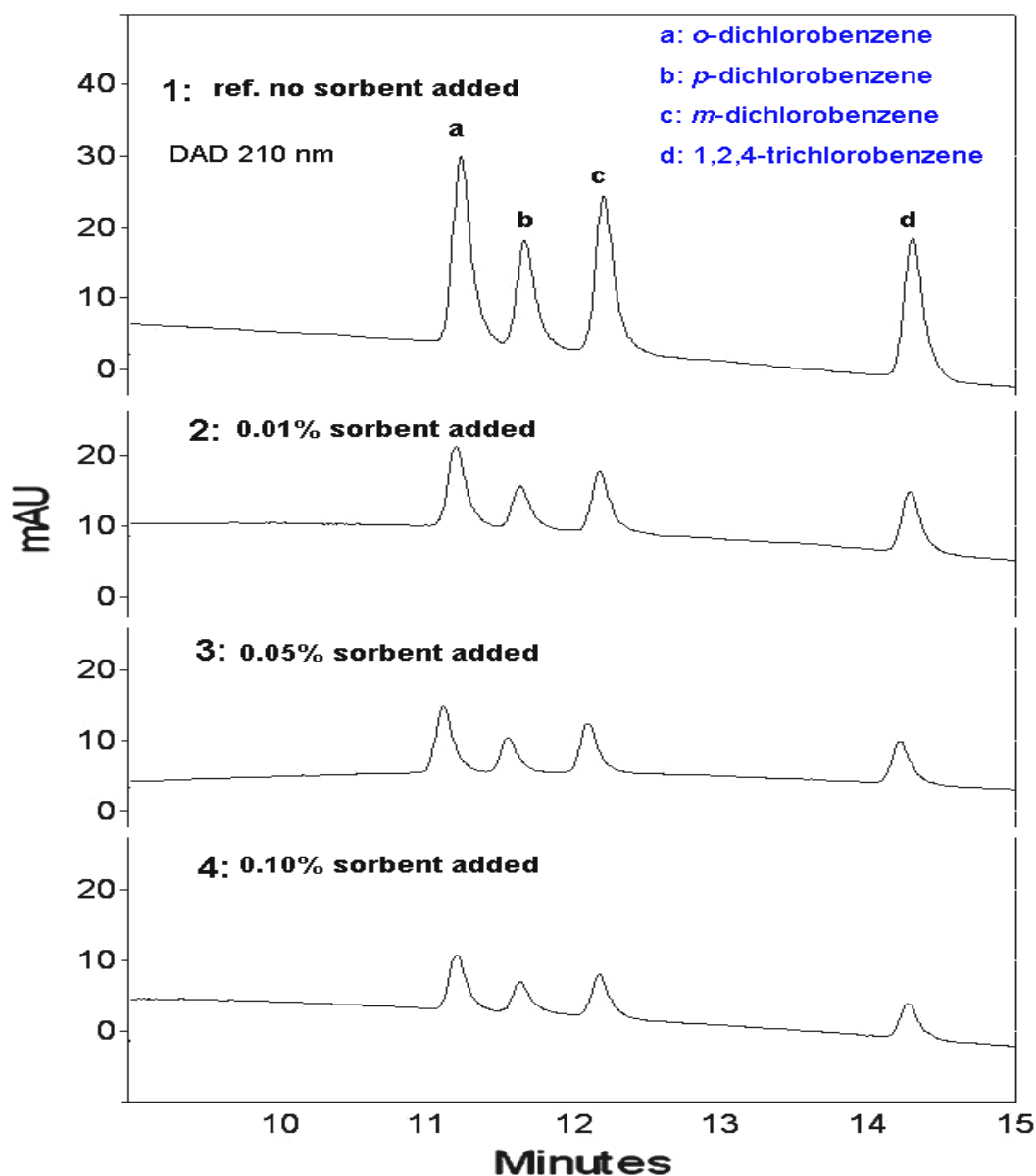
**Fig. S10** Effect of the adsorption time on the decolorization rate of 0.040 mM MB (A) and 0.030 mM BV (B) in the presences of the BaSO<sub>4</sub>-SDBS inclusion adsorbent (0.03%) (curve 1) and activated carbon (0.03%) (2).



**Fig. S11** A: Treatment of a dye wastewater with 230,000 times the color density and 3800 mg/l COD. 1: variation in color and 2: variation COD; the hybrid adsorbent was added from 1 to 6%. B: Treatment of a chlorobenzene chemical wastewater. a: *o*-dichlorobenzene, b: *p*-dichlorobenzene, c: *m*-dichlorobenzene and d: 1,2,4-trichlorobenzene. The hybrid adsorbent was added from 0 to 0.10%.



**Fig. S12** Effect of the addition of adsorbent on the leaching rate of SDBS



**Fig. S13** Determination of four chlorobenzene compounds in the wastewater treated with the BaSO<sub>4</sub>-SDBS inclusion adsorbent. 1: no adsorbent and 2: 0.01%, 3: 0.05% and 4: 0.10% adsorbent was added, respectively. The HPLC measurement of *o*-dichlorobenzene (a) *p*-dichlorobenzene (b), *m*-dichlorobenzene (c) and 1, 2, 4-trichlorobenzene (d) were carried out at 210 nm with DAD detector, where the gradient elution was carried out from 55% deionized water and 45% acetonitrile at the beginning to 15% and 85% at 15 min, and then to 10% and 90% at 18 min. 20  $\mu$ l of a supernatant was injected and the flow rate of the mixed mobile phase 1.0 ml/min.