Supporting Information

Selective desorption characteristics of halloysite nanotubes for anonic azo dyes

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MATERIALS

Halloysite powder was supplied from Xintai Benyuan Clay co., China. Methyl orange and Congo red were purchased from Sigma-Aldrich and used as received. Other reagents were of analytical grade.

METHODS

Adsorption experiments. 0.1 g of clay powder were added into 50 ml of 300 mg/L dye solution (pH=7). The mixture was shaken for 24 h (120 rpm/min) at 20 ^{o}C. This time was long enough to ensure that adsorption equilibrium can be reached. Then, the mixture was centrifuged and the supernatant was analysed to determine remaining dye concentration by UV-Vis spectrophotometer at 460 nm and 500 nm for methyl orange and Congo red, respectively. The adsorption capacity of the adsorbent was calculated by the difference between initial and final dye solution concentrations.

Repeated adsorption–desorption experiments. After centrifugation, the supernatant was discarded. 50 ml of deionized water was added into the dye-loaded adsorbent and

sufficiently dispersed. Then the mixture was placed in oscillator and stirred at 20 ^{o}C for 24 h. Thereafter, the supernatant obtained by centrifugation was measured to determine dye concentration. The above procedure was repeated three times to ensure adequate removal of the dye molecules. The total amount of desorption is the sum of three desorption data. Whereafter, 50 ml of 300 mg/L dye solution was added into centrifuge tubes to be adsorbed by the samples again. Five times of the above adsorption-desorption process were carried out.

CHARACTERIZATION

The samples were characterized by different approaches like colorimetric test, X-ray diffraction (XRD), UV–visible spectra, transmission electron microscopy (TEM), thermogravimetric analysis and ^{1}H NMR. The color properties of the HNTs and hybrids were estimated in terms of the CIE $L^*a^*b^*$ system using a NH310 3nh High-Quality Colorimeter. The XRD patterns of the samples were recorded using a Philips X-ray diffraction instrument operating at 40 kV and 40 mA with filtered Cu Kα radiation (n = 1.5418 Å). UV–visible spectra in diffuse reflectance mode of the samples were collected using a S-4100 UV-vis spectrophotometer in the 800–200 nm range. FEI Tecnai G20 transmission electron microscope was used for observing structure and morphology of the samples. Thermogravimetric analysis (TG-DTG) was performed on a SDT Q600 thermal analyser. Approximately 6 mg of the sample was heated from room temperature to 800 ^{o}C with a heating rate of 10 ^{o}C / min. ^{1}H NMR spectra of the Congo red and the hybrids were recorded on Bruker 400M NMR using TMS as an internal standard.

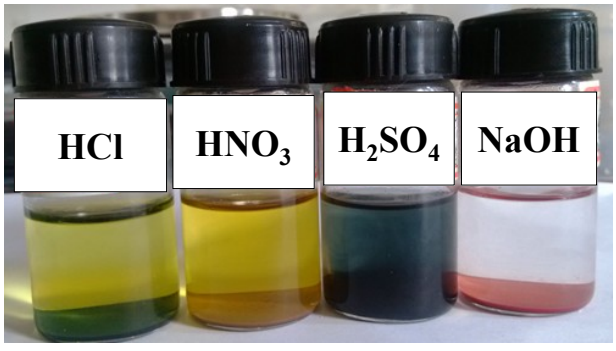

Figure S1. The photograph of Congo red/halloysite hybrid immersed for 24 h in strong acids and base solutions.

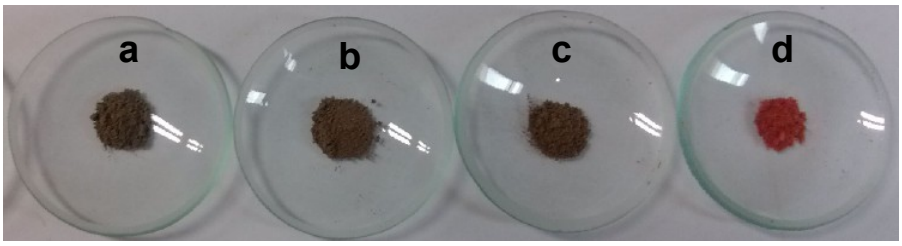

Figure S2. The photograph of Congo red/halloysite hybrid after 24 h chemical attack with concentrated HCl (a), HNO_3 (b), H_2SO_4 (c), and 4 M NaOH (d).

Table S1

Color characteristics of the samples.

Sample	Color coordinates		
	*L**	*a**	*b**
Hybrid	51.38	16.39	10.53
HCl-treated hybrid	53.38	0.46	2.84
HNO_3-treated hybrid	52.47	1.86	4.02
H_2SO_4-treated hybrid	51.10	2.49	4.49
NaOH-treated hybrid	52.85	17.79	10.97

*L**, lightness; *a**, red-green index; *b**, yellow-blue index.

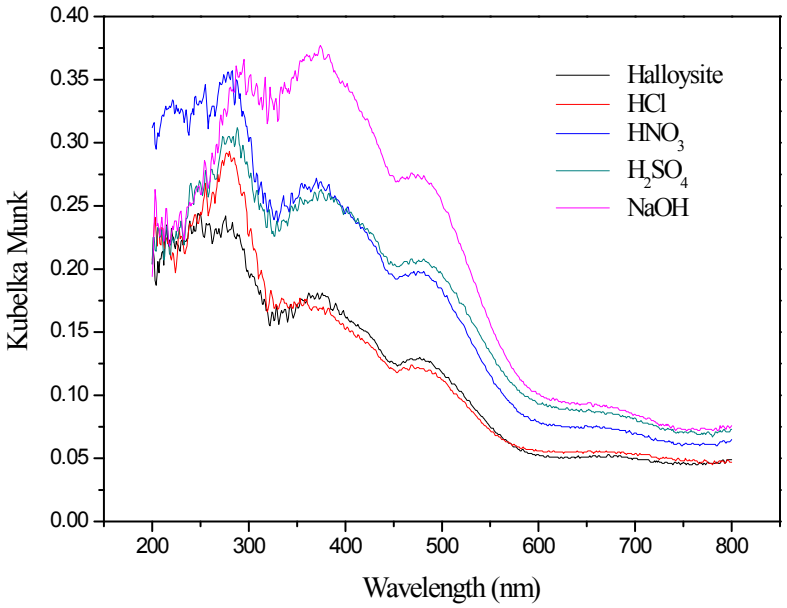

Figure S3. UV–vis spectra of natural, strong acid- or base-treated halloysite.

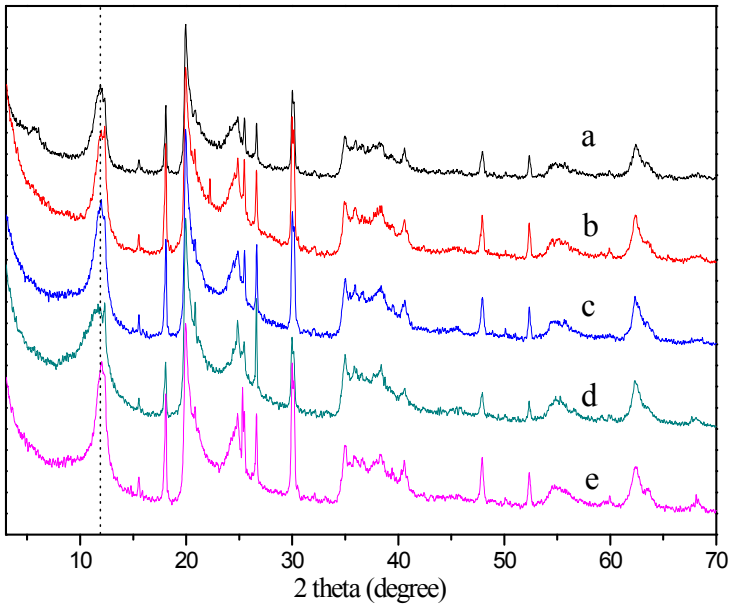

Figure S4. XRD patterns of natural halloysite (a), the blank samples after 24 h chemical treatment with concentrated HCl (b), HNO_3 (c), H_2SO_4 (d), and 4 M NaOH (e).

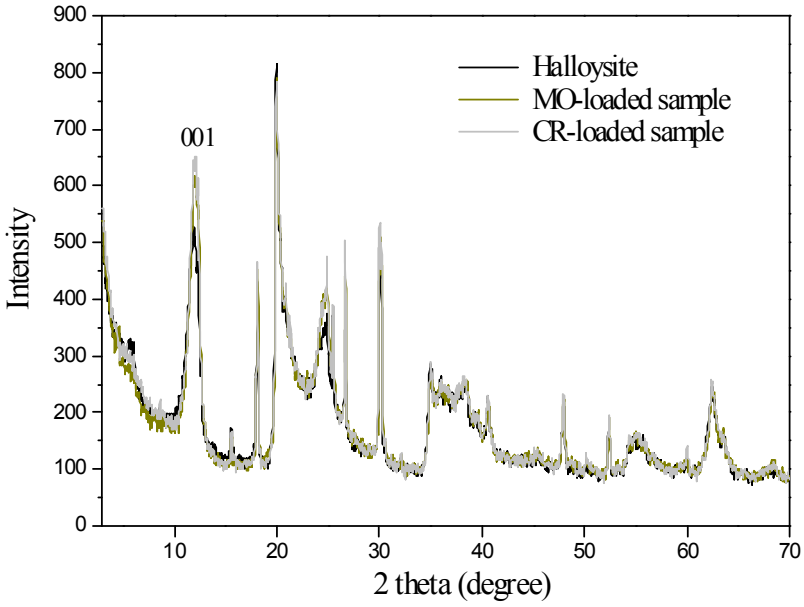

Figure S5. XRD patterns of natural and dye-loaded halloysites.

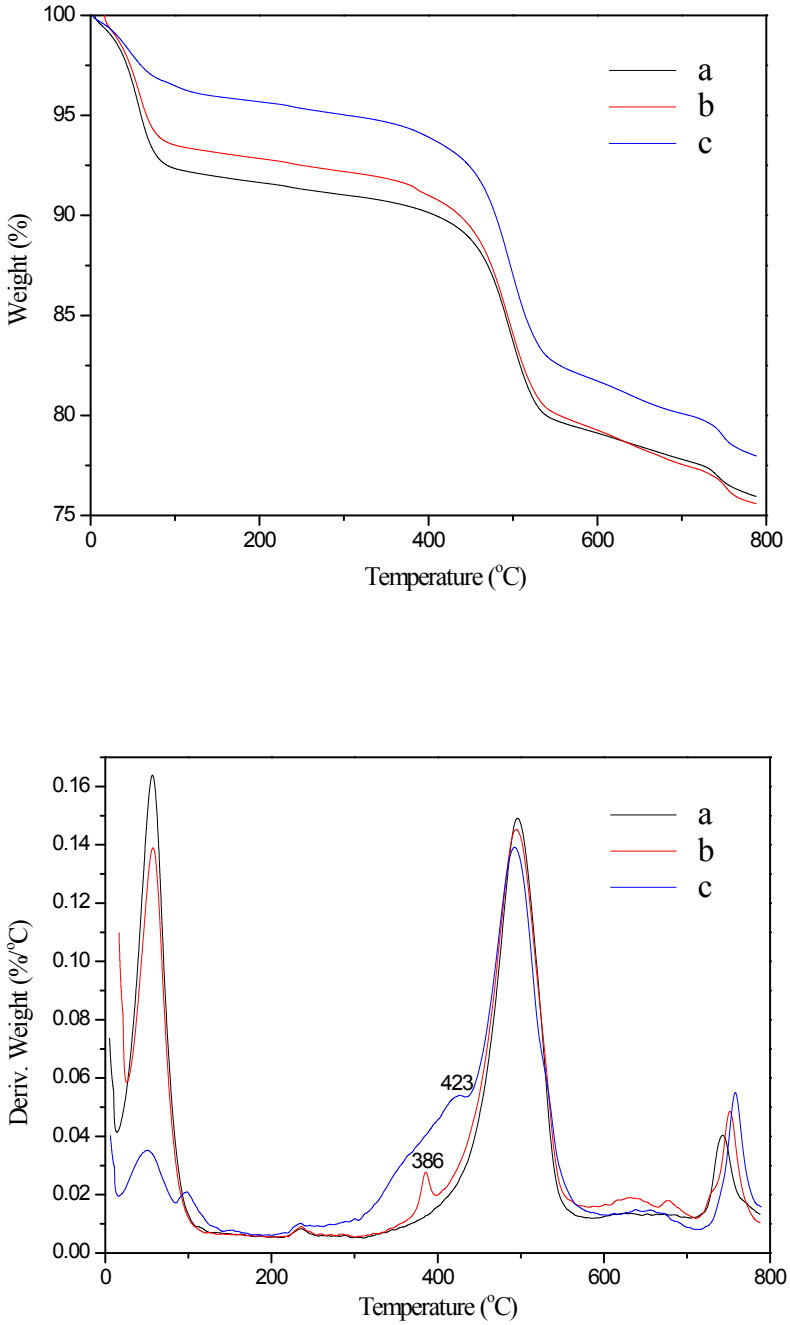

Figure S6. TG and DTG curves of halloysite clay (a), physically grinded sample (According to 25.9 mg/g of the adsorption capacity of halloysite for methyl orange, halloysite powders were mixed and hand-ground in an agate mortar with certain quantity (2.59 wt.%) of methyl orange dye) (b), dye-loaded sample in the condition of 300 mg/L of methyl orange solution (c).

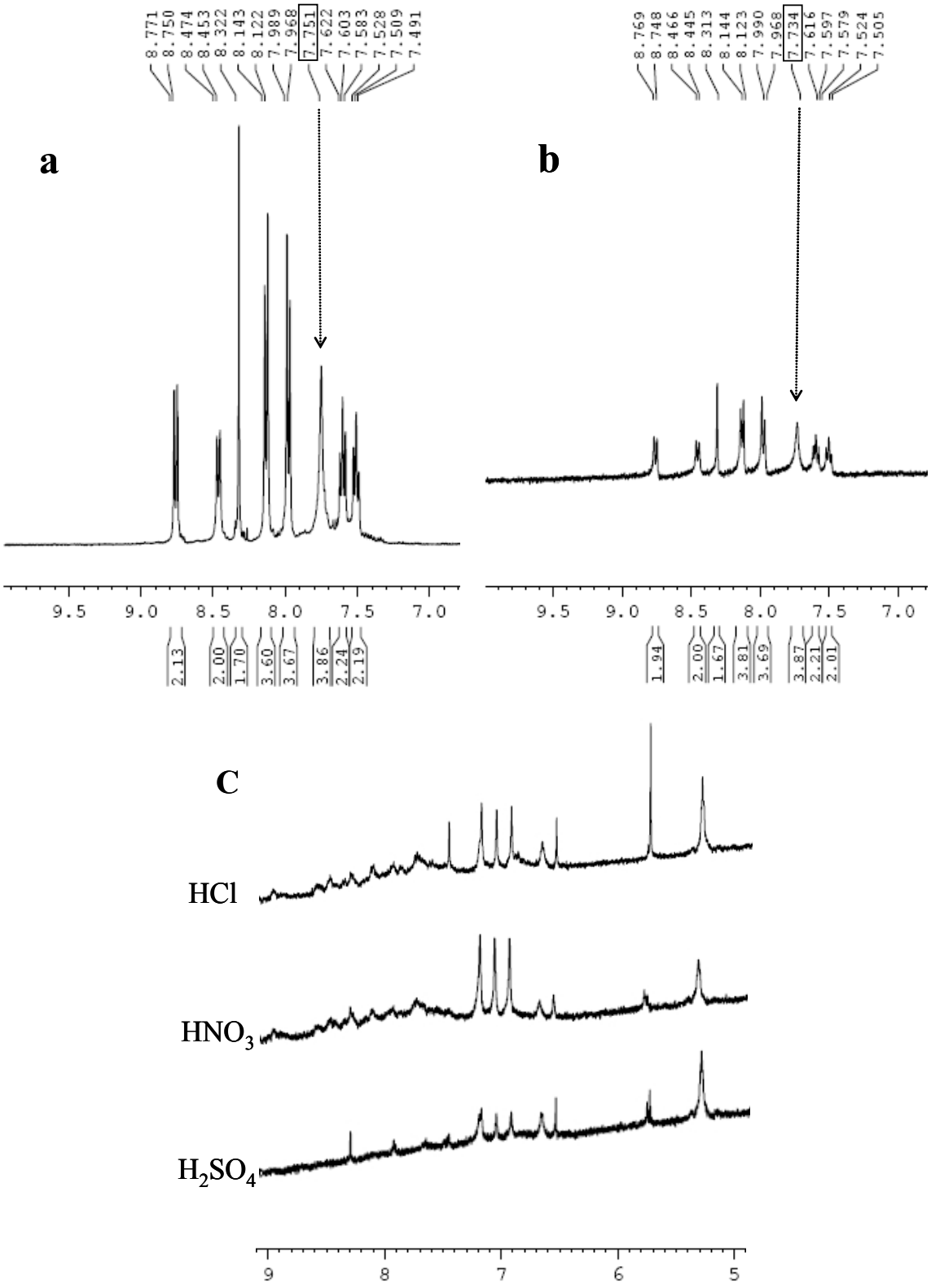

Figure S7. ^{1}H NMR spectra of Congo red (a) , Congo red/halloysite hybrid (b) and acid-treated samples (c).

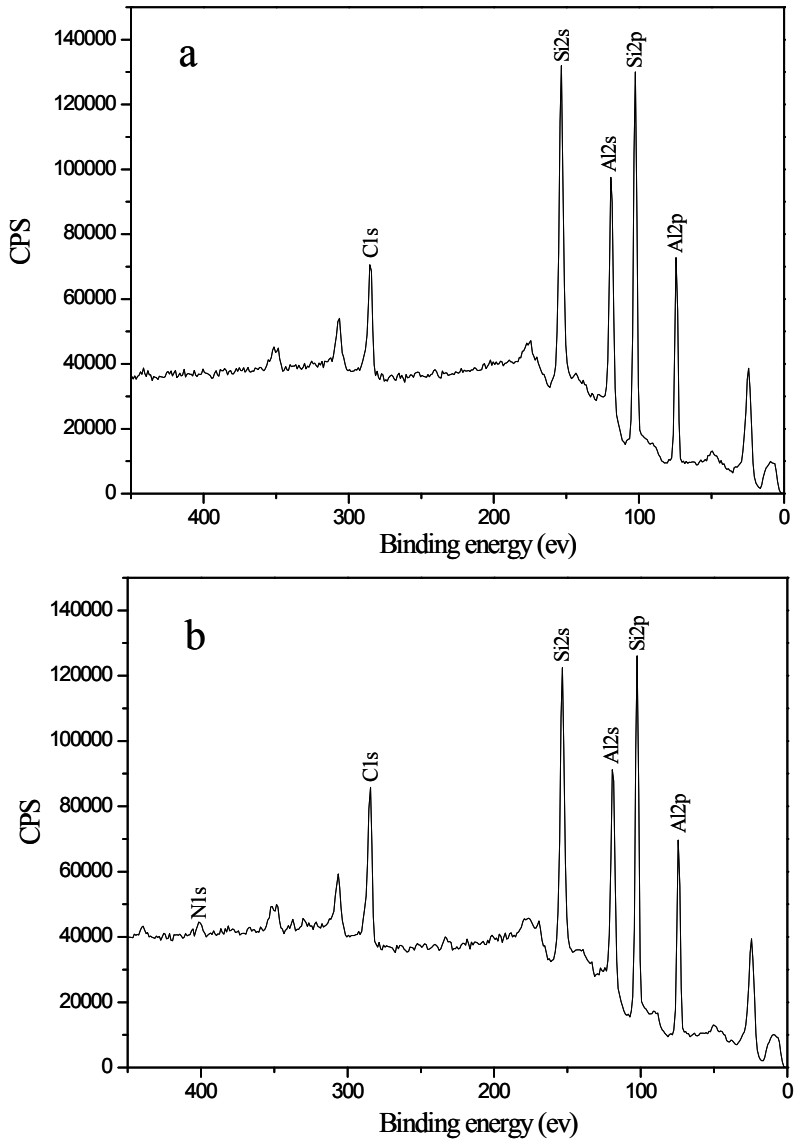

Figure S8. XPS spectra of halloysite (a) and Congo red/halloysite hybrid (b).

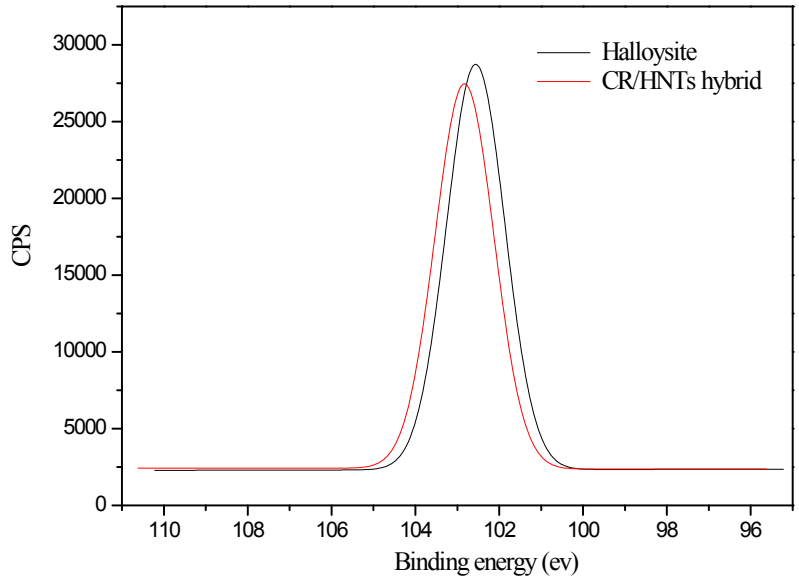

Figure S9. Si_{2p} detail spectra of halloysite and Congo red/halloysite hybrid.