Electronic Supporting Information

A facile one-pot method for synthesis of low-cost magnetic carbon nanotubes and their applications for dye removal

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Experiment

Batch adsorption experiments

Dye concentration was determined colorimetrically by measuring at maximum absorbance of the dyes (λ_{max} =530 nm for neutral red, λ_{max} =552 nm for Rhodamine B, λ_{max} =616.9 nm for malachite green, λ_{max} =488 nm for congo red and λ_{max} =631 nm for methylene blue). Calibration curve was plotted between absorbance and concentration of the dye to obtain the absorbance-concentration profile of dyes. Batch adsorption experiments were conducted in 50 ml glass bottles with 30 mg APCNTs or MAPCNTs and 40 ml dye solution of different initial concentrations of 70~140 mg/L for neutral red, 10~70 mg/L for Rhodamine B, 50~110 mg/L for malachite green, 30~100mg/L for congo red and 60~130 mg/L for methylene blue. Sample bottles were shaken on a shaker (TS-2102C, Shanghai Tensuclab Instruments Manufacturing Co., Ltd., China) and operated at a constant temperature of 25 °C and 150 rpm for 2 hours. Preliminary experiments indicated that the adsorption of dye reached equilibrium in about 1.5 hours. Thus, the contact time of 3 hours was selected in the batch experiments. All the adsorption experiments were conducted in duplicates, and only the mean values were reported. The maximum deviation for the duplicates was usually less than 5%. The blank experiments without the addition of APCNTs or MAPCNTs were conducted to ensure that the decrease in the concentration was actually due to the adsorption of APCNTs or MAPCNTs, rather than by the adsorption on the

glass bottle wall. After adsorption equilibrium has been achieved, the dyes concentration of the solutions was measured using a spectrophotometer (UV759UV-VIS, Shanghai Precision & Scientific Instrument Co. Ltd.). The initial pH was adjusted using HCl or NaOH solution.

The amount of adsorbed dyes on adsorbents (q_t , mg/g) was calculated as follows:

$$q_t = (C_0 - C_t) \times \frac{V}{m} \tag{1}$$

Where c_0 and c_t are the dye concentrations at the beginning and after a period of time (mg/L),

V is the initial solution volume (L); and m is the adsorbent weight (g). The amount of adsorbed dye per unit weight of adsorbents (mg/g) was plotted versus the equilibrium concentration (mg/L).

Data analysis

Langmuir model

The form of the Langmuir isotherm can be represented by the following equation:

$$q_e = q_m \frac{K_L C}{1 + K_L C} \tag{2}$$

where q_e is the amount of dye adsorbed per gram of adsorbent (mg/g), *C* denotes the equilibrium concentration of dye in solution (mg/L); K_L represents the Langmuir constant (L/mg) that relates to the affinity of binding sites and q_m is a theoretical limiting adsorption capacity when the monolayer surface is fully covered with dye molecules and assists in the comparison of adsorption performance (mg/g). Another important parameter, R_L , called the separation factor or equilibrium parameter, which can be used to determine the feasibility of adsorption in a given concentration range over adsorbent, also evaluated in this study, was determined from the relation¹:

$$R_L = \frac{1}{1 + K_L C_0} \tag{3}$$

where K_L is the Langmuir adsorption constant (l/mg) and C_0 is the initial dye concentration (20mg/l). Ho and McKay² established that (1) $0 < R_L < 1$ for favorable adsorption, (2) $R_L > 1$ for unfavorable adsorption, (3) $R_L = 1$ for linear adsorption and (4) $R_L = 0$ for irreversible adsorption. Freundlich model

The Freundlich isotherm model has the following form:

$$q_e = K_F C^{1/n} \tag{4}$$

where q_e is the amount of dyes adsorbed per gram of adsorbent (mg/g); *C* is the equilibrium dye concentration in solution (mg/L); K_F and *n* are the Freundlich constants, which represent the adsorption capacity and the adsorption strength, respectively. The magnitude of 1/n quantifies the favorability of adsorption and the degree of heterogeneity of the adsorbent surface.

Dubinin-Radushkevich (D-R) model

The D-R isotherm model has the following form:

$$\ln q_e = \ln q_m - B\varepsilon^2 \tag{5}$$

B, a constant related to the mean free energy of adsorption (mol²/kJ²); q_m , the theoretical saturation capacity; and ε , the Polanyi potential, which is equal to

$$\varepsilon = RT\ln(1 + \frac{1}{C}) \tag{6}$$

where *R* (J·mol⁻¹·K⁻¹) is the gas constant and *T* (K) is the absolute temperature. For D-R isotherm model, from *B* values the mean energy of adsorption, *E*, can be calculated using the relation³

$$E = \frac{1}{\sqrt{-2B}} \tag{7}$$

Based on equations (5), (6) and (7), the isotherm constants, *E* and determination coefficients were calculated. The mean energy of adsorption (E) is the free energy change when one mole of ions is transferred from infinity in the solution to the surface of the solid. When one mole of ions is transferred, its value is in the range of $1-8 \text{ kJ} \cdot \text{mol}^{-1}$ for physical adsorption⁴. The value of E is between 8 and 16 kJ·mol⁻¹ for an adsorption process by ion-exchange. A value of E in the range of 20-40 kJ·mol⁻¹ is indicative of chemisorption⁵.



Figure S1 XRD patterns of APCNTs and MAPCNTs.

The XRD patterns of APCNTs and MAPCNTs are shown in Fig. S1, which indicate that the MAPCNTs were a mixture of two phases: Fe and CNTs. The diffraction peak at $2\theta=26.2^{\circ}$ is assigned to (002) plane of CNTs, and the diffraction peak at $2\theta=44.6^{\circ}$ is assigned to (110) plane of Fe and (101) plane of CNTs; the two peaks corresponding to the structure of APCNTs also exist in the XRD pattern of the MAPCNTs. No other peaks corresponding to impurities were detected after NaClO modification.



Figure S2 Raman spectra of APCNTs and MAPCNTs.

The Raman spectra of APCNTs and MAPCNTs are shown in Fig. S2. No peaks have been found in the low frequencies (100~800 cm⁻¹), which indicates that no iron oxide exists in APCNTs or MAPCNTs. In APCNTs or MAPCNTs samples, because iron nanoparticles are encapsulated by graphitic shells and iron has only one atom in the primitive unit cell, no optical-branch zero wavevector vibrational modes exist and the Raman peak of iron is difficult to be tested⁶. The *G* peak at 1,585 cm⁻¹ is related to E_{2g} graphite mode^{7.9}. The strong intensity of this peak indicates good graphitization of CNTs. The D peak at around 1,345 cm⁻¹ is induced by defective structures, which could include minor amorphous carbon and some graphite particles seen in the sample (Fig. 1). G' band and weak structures arising from double resonance processes are observed in the second-order region of the spectra. The intensity ratio of the G and D peaks (I_G/I_D) is an indicator of the structure quality of CNT sample. As shown in Fig. S2, the higher I_G/I_D ratio means a higher structure quality of CNTs due to the removal of amorphous carbon after NaClO modification.



Figure S3 Thermal analysis curve of the APCNTs and MAPCNTs.

The TGA curves of APCNTs and MAPCNTs exhibit two main weight loss regions as shown in Fig. S3. APCNTs and MAPCNTs are considerably stable and show a little weight loss close to 5% below 200 °C in the first region, which can be attributed to the evaporation of adsorbed water and the elimination of carboxylic and hydroxyl groups on the CNTs wall. The rapid weight loss region can be due to the oxidation of carbon in the CNTs. The final weight of the remaining samples is 23.4 % (APCNTs) and 26.6 % (MAPCNTs) of the original weight. Assuming that the final material is Fe₂O₃, the quantity of Fe in the APCNTs can be estimated to be 16.38 %, which is much lower than that in the MAPCNTs (18.62 %). The temperatures at which the main thermal events took place during the entire oxidation process may be identified from the DTA curves (Fig. S3). Comparing APCNTs with MAPCNTs, it is clearly seen that the main thermal events temperature (T_m) decreased from ~470 to ~450°C, which may be attributed to the CNTs structure defects and more oxygen-containing functionality produced by NaCIO modification. However, the thermal events temperature is so high that MAPCNTs could meet the application needs of adsorbent in water treatment.



Figure S4 The optical images of dispersion properties of the APCNTs and MAPCNTs in water with a concentration of 0.5 mg mL⁻¹ after several days storage.



Figure S5 (a) Langmuir, (b) Freundlich, (c) D-R isotherms for dye adsorption onto MAPCNTs.

Sample	SSA	ESA	ISA	PV	APD	0%			
APCNTs	165.7	161.6	4.1	0.39	9.86	2.88			
MAPCNTs	186.3	186.3	0	0.53	11.89	7.15			
Note: SSA=special	surface ar	rea $(m^2/g);$	ESA=E:	xternal sur	face area	(m ² /g);			
ISA=Internal surface area (m ² /g); PV= pore volume (cm ³ /g); APD=average pore									
diameter (nm); O%: surface oxide (at. %) by XPS;									

Table S1 Pore structures and oxygen content of APCNTs and MAPCNTs

Adsorbate	Langmuir model				Freundlich model			Dubinin-Radushkevich model			
	$q_m(mg/g)$	$K_L(l/mg)$	R_L	R^2	K_F	n	R^2	$B(mol/kJ^2)$	$Q_m(mg/g)$	E(kJ/mol)	R^2
Neutral red	107.53	2.90	0.0047	0.999	82.4	11.05	0.920	6.58E-10	0.000541	27.56	0.941
Methylene blue	101.63	0.43	0.0332	0.991	52.6	5.52	0.919	1.418E-9	0.000639	18.78	0.996
Malachite green	94.34	1.19	0.0167	0.993	60.1	7.03	0.979	9.36E-10	0.000429	23.10	0.960
Congo red	67.57	0.25	0.1064	0.975	28.8	4.78	0.935	1.476E-9	0.000209	18.40	0.960
Rhodamine B	46.08	1.31	0.0736	0.991	21.2	4.05	0.575	1.119E-9	0.000196	21.13	0.996

Table S2. Langmuir, Freundlich, and D-R isotherms parameters of MAPCNTs adsorbents

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