



Magnetic removal of dyes from aqueous solution using multi-walled carbon nanotubes filled with Fe₂O₃ particles

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ABSTRACT

The Fe₂O₃ nanoparticles have been introduced into the multi-walled carbon nanotubes (MWCNTs) via wet chemical method. The resulting products are characterized by TEM, EDX, XRD and VSM. The magnetic MWCNTs have been employed as adsorbent for the magnetic separation of dye contaminants from water. The adsorption test of dyes (Methylene Blue and Neutral Red) demonstrates that it only takes 60 min to attain equilibrium and the adsorption capacities for Methylene Blue and Neutral Red in the concentration range studied are 42.3 and 77.5 mg/g, respectively. The magnetic MWCNTs can be easily manipulated in magnetic field for desired separation, leading to the removal of dyes from polluted water. The integration of MWCNTs with Fe₂O₃ nanoparticles has great potential application to remove organic dyes from polluted water.

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1. Introduction

Dyes are widely used in various fields, and their discharge into water causes environmental pollution. Most of the used dyes are stable to photodegradation, bio-degradation and oxidizing agents [1]. From an environmental point of view, the disposal of synthetic dyes is of great concern, since dye effluents are aesthetic pollutants and can be toxic to organisms and mammals. Methylene Blue (MB) and Neutral Red (NR) are two kinds of cationic dyes which are used extensively in the industries. Their effluents are aesthetic pollutants which can reduce light penetration and photosynthesis. In addition, they are chemicals that exhibit toxic effects toward microbial populations [2]. Conventional physicochemical and biological treatment methods are ineffective for their removal because they have enough stability. Therefore, the adsorption process becomes the one of the efficient methods to remove these dyes from effluent and carbon materials are the most widely used adsorbents for this purpose.

Carbon nanotubes (CNTs) have been the focus of an intensive study due to their excellent mechanical, electrical, thermal properties since their discovery by Iijima in 1991 [3]. Because of their relatively large specific area, CNTs have attracted researchers' interest as a new type of powerful solid-phase extraction adsorbent.

More recently, Long and Yang [4] reported that MWCNTs could be more efficient for the removal of dioxin than activated carbon. Cai et al. [5] prepared a CNT-packed cartridge for the solid-phase extraction of compounds such as bisphenol A and 4-c-nonylphenol in environmental water samples. Li et al. [6,7] found that after oxidation with nitric acid, CNTs showed exceptional adsorption capability and high adsorption efficiency for Cd²⁺, Cu²⁺ and Pb²⁺ removal from water. The above-mentioned work suggests that CNTs may have great application potential as an effective adsorbent for the removal of organic and inorganic contaminants in environmental protection. However, until now little study is done on adsorption of dyes to CNTs [8]. Moreover, the poor solubility of CNTs and the difficulty in collecting them from their dispersing media can cause much inconvenience in their practical application. Therefore, it is necessary to explore functionalized CNTs that are able to fully disperse in aqueous media and can be easily separated from the medium. To our knowledge, however, the functionalizations of CNTs to meet the two requirements simultaneously have rarely been reported.

In this work, a simple and efficient route to introduce iron oxide nanoparticles into MWCNTs by wet chemical method is established. Since the application of magnetic particle technology to solve environmental pollution has received considerable attention in recent years [9], MWCNTs filled with magnetic particles could be a good choice to make the best use of the advantages of CNTs. Magnetic MWCNTs can be used to adsorb contaminants from aqueous effluents and, after adsorption, can be separated from the medium by

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a simple magnetic process. The test of adsorption of dyes to CNTs is also the topic of the present work. MB and NR are used to test the adsorption of magnetic MWCNTs and satisfactory results are observed.

2. Experimental

2.1. Materials and methods

The carbon nanotubes used here had an inner diameter about 10 nm and an outer diameter in the range of 40–60 nm (with lengths of up to a few microns), which were purchased from Nanoport Co. Ltd. (Shenzhen, China). $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was purchased from Shanghai chemical company. Analytical grade MB and NR were used to prepare stock solutions of 500 mg/L of the two dyes, which were further diluted to the required concentrations before use.

Transmission electron microscopy (TEM) micrographs of sample were taken using a JEM-2011 electron microscope (JEOL, Japan), with an accelerating voltage of 200 kV. Energy-dispersive X-ray (EDX) spectrometry was carried out with spectroscopy (Oxford, INCA) attached to TEM. XRD measurement was performed on a Rigaku D/max-rB X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.1542 \text{ nm}$). The magnetic property was measured by vibrating sample magnetometer (VSM) (model 7400, Lakeshore Company, USA).

2.2. Introduce magnetic particles into MWCNTs

In a typical synthesis, firstly, MWCNTs were purified by refluxing in 3 mol/L HNO_3 for 24 h. The purified MWCNTs were chemically shortened by sonication in a mixture (3:1) of concentrated sulfuric acid (98%) and nitric acid (70%) for 8 h [10]. Then the samples were washed with water. Based on Wilson's method [11], the ferric nitrate liquid was sucked into the tubes in the similar way. Briefly, acid treated MWCNTs (50 mg) were stirred with 50 mL of saturated ferric nitrate for 12 h, filtered and washed with water, then dried in air at room temperature. The sample was then heated under an argon atmosphere at a rate of 4°C min^{-1} from room temperature to 450°C and kept at this temperature for 6 h.

2.3. Adsorption experiments

The specific surface area and pore size distributions of acid treated MWCNTs and magnetic MWCNTs were measured by nitrogen adsorption/desorption at 77 K using a Micromeritics Tristar 3000 automatic physisorption instrument. The Brunauer, Emmett and Teller (BET) theory is the commonly used method for the determination of the specific surface area of sample. The specific surface area of the sample is determined by physical adsorption of a gas on the surface of the solid and by measuring the amount of adsorbed

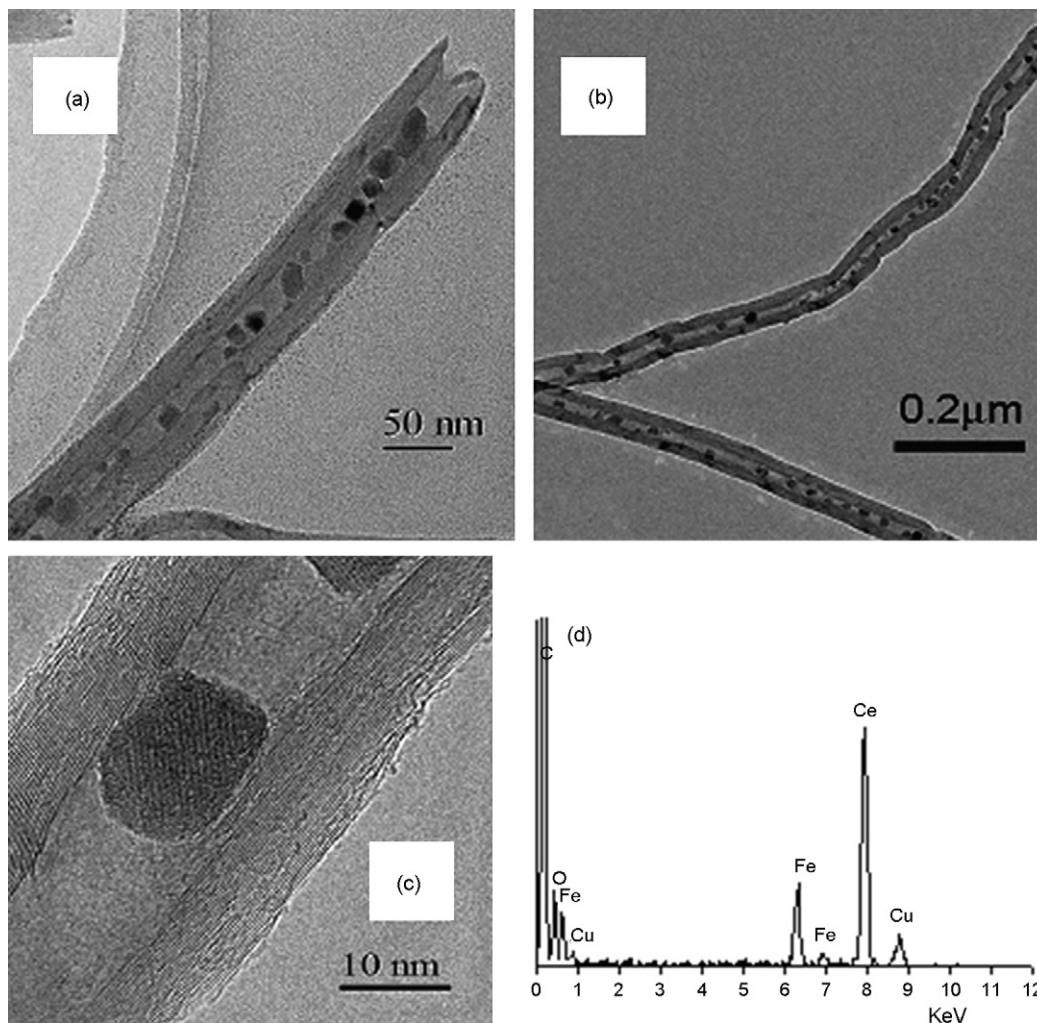


Fig. 1. (a–c) TEM images of carbon nanotubes filled with $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. (d) EDX spectrum of carbon nanotubes filled with $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles.

gas corresponding to a monomolecular layer on the surface. The data are treated according to the BET theory.

Adsorption experiments were carried out in glass bottles at 25 °C. 50 ml of dye solution of known initial concentration was shaken with 0.05 g magnetic MWCNTs on a shaker at 200 rpm. The initial pH values of the solutions were adjusted with 0.1 M HNO₃ or NaOH using pH meter. After magnetic separation using the permanent magnet, the equilibrium concentrations of dyes were measured with a UV–vis spectrophotometer (Hitachi Model U3010) at appropriate wavelengths corresponding to the maximum absorbance of each dye, 664 and 530 nm for MB and NR, respectively. The amount of dye adsorbed was calculated using the equation [12]:

$$q_e = (C_0 - C_e) \frac{V}{m} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of dye (in mg/L), M is the mass of magnetic MWCNTs (g), and V is the volume of solution (L).

3. Results and discussion

3.1. MWCNTs filled with γ -Fe₂O₃

TEM images presented in Fig. 1 demonstrated that the tip of MWCNTs was opened and the inside of the nanotubes were filled with in-situ produced Fe₂O₃ nanoparticles. Ferric nitrate solution was sucked into the carbon nanotubes due to capillary forces during the impregnation process. This was reasonable because the surface tension of water (72 mN m⁻¹) is sufficiently low (i.e. <190 mN m⁻¹) to allow wetting and filling of nanotubes [13]. The purification and oxidation treatment of MWCNTs in concentrated acid contributed to the formation of open tips and surface functional groups, which were beneficial to the entrance of iron ion by capillarity as well as the adsorption and nucleation of iron inside nanotubes.

Under our experimental conditions, the oxide precursor (ferric nitrate) accumulated inside the tubes were decomposed into Fe₂O₃ crystallites during calcination at 450 °C while iron ion adsorbed and nucleated on the outer surface of tubes were removed easily by washing before calcination. Thus the majority of Fe₂O₃ nanoparticles was present inside the nanotubes and found rarely on the outside wall of nanotubes. In comparison with Green's method [14] that the preparation of NiO inside nanotube by refluxing nickel precursor in strong acid, our experimental condition is mild but similar phenomena is observed.

The high-resolution transmission electron microscopy (HRTEM) image of the particles inside MWCNTs (Fig. 1c) shows that the shape of some particles looks like cubes with a visible lattice, implying the high crystallinity of these maghemite particles.

The average size of the particles estimated from TEM observation is about 10 nm. The growth of the Fe₂O₃ crystallites may be controlled by the surface structure of the internal walls due to the spatial constraints and the shape of the Fe₂O₃ crystallites may reflect their surface-wetting properties. Because of the evolution of gases (NO₂, H₂O) during calcination, Fe₂O₃ particles could not form the nanowire continuously.

The chemical composition of the nanoparticles inside carbon nanotubes was analyzed by EDX. The EDX spectrum (Fig. 1d) shows iron, oxygen, carbon and copper. It is obvious that the copper peak is caused by the copper grid used to clamp the nanoparticles. The carbon comes from carbon nanotube. EDX quantitative microanalysis indicates the presence of carbon (82.2%), oxygen (7.6%) and iron (10.1%) in the magnetic MWCNTs.

The X-ray diffraction (XRD) pattern of magnetic MWCNTs was displayed in Fig. 2. It is obvious that the peak at 2 θ values of 26.2° is

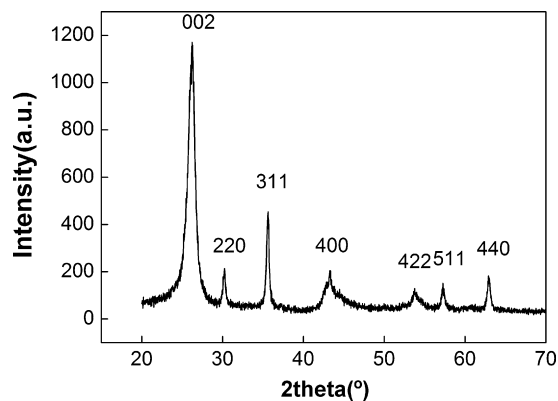


Fig. 2. The XRD pattern of magnetic MWCNTs.

caused by the carbon nanotubes while the other diffraction peaks correspond to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) suggests the presence of γ -Fe₂O₃ as the magnetic phase in MWCNTs [15]. The magnetic phase was further confirmed by XPS (Fig. 3). The positions of the Fe (2p_{3/2}) and Fe (2p_{1/2}) peaks are marked at 711.3 and 724.4 eV, respectively, which are in good agreement with the values reported for γ -Fe₂O₃ in the literature [16]. This strongly suggests the formation of γ -Fe₂O₃ in the composites.

The magnetic properties of the MWCNTs impregnated with γ -Fe₂O₃ were studied by VSM. Fig. 4a shows the hysteresis loop between ± 10 kOe at 300 K, which has a saturation magnetization of 2.5 emu/g and exhibits the superparamagnetic characteristic. It has been suggested that bulk γ -Fe₂O₃ is ferromagnetic at room temperature. However, it becomes superparamagnetic due to the smaller size of Fe₂O₃ particles [16]. The prepared magnetic MWCNTs can be readily dispersed in water and form a stable dispersion (Fig. 4b). In the procedure of vigorous acid treatment previously, the hydrophilic groups (i.e. carboxylic groups) can be introduced onto the sidewall of MWCNTs, thus enhancing the solubility and dispersion of MWCNTs in solution [17]. Moreover, magnetic MWCNTs respond rapidly to the permanent magnet. As shown in Fig. 4c, it can be easily attracted from water solution by an external magnetic field. The redispersion and separation process can be repeated readily, which makes it possible to conveniently manipulate MWCNTs by the application of an external magnetic field. The functionalized MWCNTs can enjoy promising magnetic applications without the drawback of Fe₂O₃ nanoparticles agglomeration and detachment from the walls of the MWCNTs due to the protection of the carbon film.

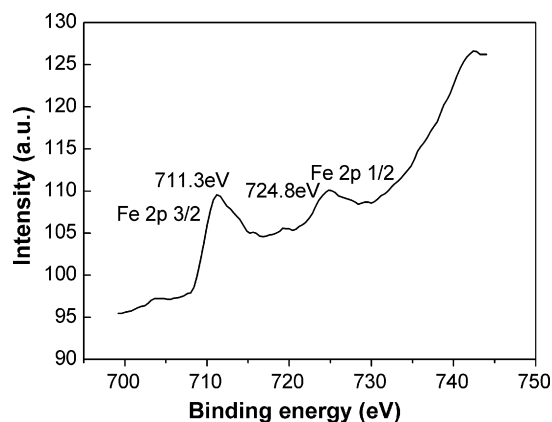


Fig. 3. The Fe 2p XPS of magnetic MWCNTs.

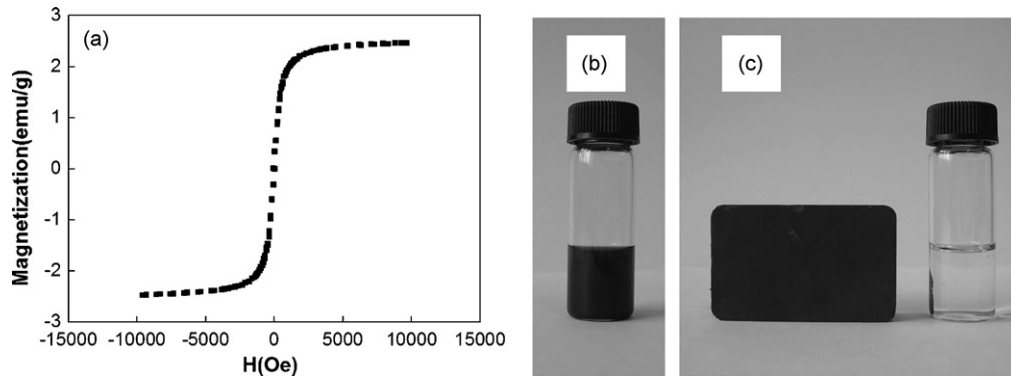


Fig. 4. (a) Magnetization curve of magnetic MWCNTs. (b) Photograph of magnetic MWCNTs dispersed in water after sonification (c) The response of magnetic MWCNTs to a magnet.

3.2. Adsorption and removal of dyes

The specific surface area and pore specific volume of acid treated MWCNTs and magnetic MWCNTs were measured. When the Fe_2O_3 particles are filled in the MWCNTs, the surface area of the sample decrease slightly from 129 to $114 \text{ m}^2 \text{ g}^{-1}$ while the microporous volume decrease from 0.355 to $0.306 \text{ cm}^3 \text{ g}^{-1}$. Because of its relatively small surface area and microporous volume, Fe_2O_3 should cause a decrease in the surface area and microporous volume compared to pure MWCNTs. The data suggest that the BET surface area and the microporous volume are not significantly affected by the presence of Fe_2O_3 in the composites.

The adsorption of dyes MB and NR from aqueous solutions onto the magnetic MWCNTs were studied. The effect of contact time on the amount of dye adsorbed was investigated at 20 mg/L initial concentration of both dyes (Fig. 5). It takes only 60 min to attain equilibrium. The short equilibrium time needed suggests that magnetic MWCNTs have high adsorption efficiency to the removal of dyes from water.

The effects of pH on adsorption percentages of dyes were investigated over the range of pH values from 3 to 10. But for NR, the experiments were only conducted from pH 3 to 7 for avoiding dye precipitation. As shown in Fig. 6, for both two dyes, the dye removal ratios are minimums at the initial pH 3. The ratios of dyes adsorb increase when pH increases from 3 to 5.5, then the dye removal ratios are not significantly altered beyond pH 6. Therefore, the pH 6 is selected for the other experiments.

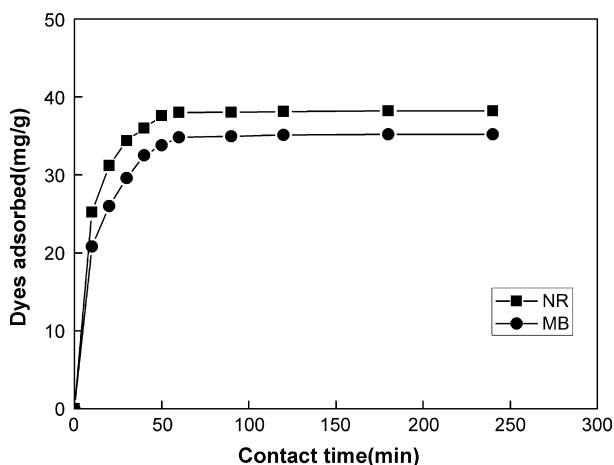


Fig. 5. The effect of contact time on the adsorption of dyes to magnetic MWCNTs ($C_0 = 20 \text{ mg/L}$, $\text{pH} = 6.0$).

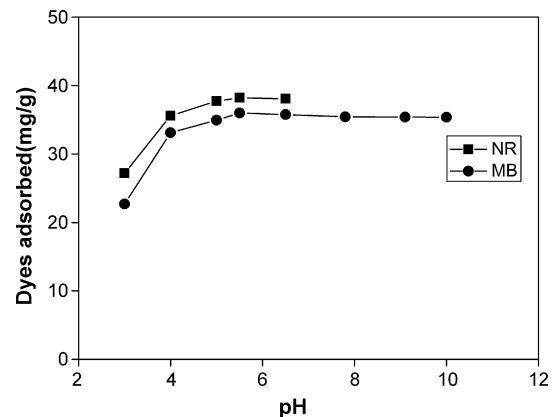


Fig. 6. The effect of pH on the adsorption of dyes to magnetic MWCNTs ($C_0 = 20 \text{ mg/L}$).

It is well known that the surface of CNTs contain some oxygen groups such as carboxylic groups ($-\text{COOH}$) and hydroxylic groups ($-\text{OH}$) after acid treatment [17]. At lower pH values, due to the protonation of electron π rich regions on the surface of MWCNTs, the positive surface charge can be formed. Under these conditions, the uptake of positive charged dyes (MB and NR) will be low. When pH increases, the carboxylic groups are ionized and the negative charge density on the surface increases, resulting in enhanced removal of dyes.

The adsorption isotherms are shown in Fig. 7. The maximum adsorption capacities for MB and NR in the concentration range studied are 42.3 g and 77.5 mg/g , respectively. The Freundlich

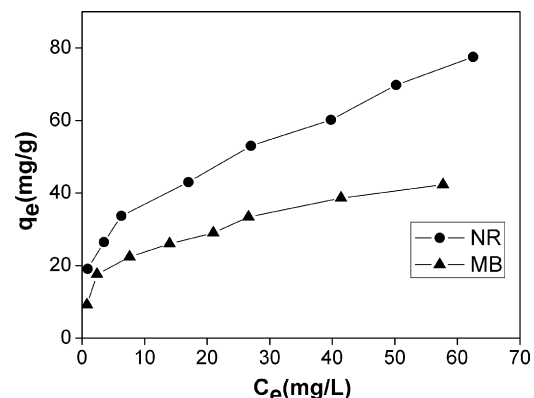


Fig. 7. Adsorption isotherms of dyes to the magnetic MWCNTs.

Table 1

Constants of Freundlich adsorption isotherm models for adsorption of dye to magnetic MWCNTs

Magnetic MWCNTs	1/n	log K	R ²
NR	0.3319	1.2668	0.986
MB	0.3278	1.0467	0.983

isotherm is used to describe the equilibrium adsorption data well. The equation is given as [12]:

$$q_e = KC_e^{1/n} \quad (2)$$

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (3)$$

where q_e is concentration of dye adsorbed (mg/g), C_e (mg/L) is the equilibrium dye concentration in the aqueous solution, K and n are constants representing the adsorption capacity and intensity of the adsorption, respectively.

As shown in Table 1, the experimental data of two dyes fit Freundlich adsorption isotherm well with correlation coefficients of 0.986 for NR and 0.983 for MB, respectively. The values of n for Freundlich isotherm are greater than 1, indicating that MB and NR are favorably adsorbed by magnetic MWCNTs [18,19].

4. Conclusion

MWCNTs filled with γ -Fe₂O₃ nanoparticles have been prepared via hydrothermal reaction of shortened MWCNTs in ferric nitrate solution and subsequent calcinations. The prepared magnetic MWCNTs can be well dispersed in the water and can be easily magnetic separated from the medium after adsorption. The adsorption capacities for MB and NR in the concentration range studied at pH 6 are 42.3 and 77.5 mg/g, respectively. It is a superior adsorbent for the removal of NR and MB from wastewater. Compared with other adsorbents, the magnetic nanotubes not only have high adsorption efficiency to dyes, but also can be easily manipulated by external magnetic field. This is a preliminary work about the removal of dyes using magnetic MWCNTs. The magnetic MWCNTs can be also employed to the removal of other pollutants. The combination of the superior adsorption properties of MWCNTs and the magnetic properties of Fe₂O₃ nanoparticles makes a powerful separation tool to deal with environmental pollution.

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References

- [1] K.R. Ramakrishna, T. Viraraghavan, Dye removal using low cost adsorbents, *Water Sci. Technol.* 36 (1997) 189–196.
- [2] R. Gong, M. Li, C. Yang, Y. Sun, J. Chen, Removal of cationic dyes from aqueous solution by adsorption on peanut hull, *J. Hazard. Mater.* 121 (2005) 247–250.
- [3] S. Iijima, Helical microtubules of graphitic carbon, *Nature* 354 (1991) 56–58.
- [4] R.Q. Long, R. Yang, Carbon nanotubes as superior sorbent for dioxin removal, *J. Am. Chem. Soc.* 123 (2001) 2058–2059.
- [5] Y. Cai, G. Jiang, J. Liu, Q. Zhou, Multiwalled carbon nanotubes as a solid-phase extraction adsorbent for the determination of bisphenol A, 4-*n*-nonylphenol, and 4-*tert*-octylphenol, *Anal. Chem.* 75 (2003) 2517–2521.
- [6] Y.H. Li, S. Wang, Z. Luan, J. Ding, C. Xu, D. Wu, Adsorption of cadmium (II) from aqueous solution by surface oxidized carbon nanotubes, *Carbon* 41 (2003) 1057–1062.
- [7] Y.H. Li, J. Ding, Z. Luan, Z. Di, Y. Zhu, C. Xu, D. Wu, B. Wei, Competitive adsorption of Pb²⁺, Cu²⁺ and Cd²⁺ ions from aqueous solutions by multiwalled carbon nanotubes, *Carbon* 41 (2003) 2787–2792.
- [8] C.H. Wu, Adsorption of reactive dye onto carbon nanotubes: equilibrium, kinetics and thermodynamics, *J. Hazard. Mater.* 144 (2007) 93–100.
- [9] L.C.A. Oliveira, R.V.R.A. Rios, J.D. Fabris, V.K. Garg, K. Sapag, R.M. Lago, Activated carbon/iron oxide magnetic composites for the adsorption of contaminants in water, *Carbon* 40 (2002) 2177–2183.
- [10] Z. Liu, Z. Shen, T. Zhu, S. Hou, L. Ying, Z. Shi, Z. Gu, Organizing single-walled carbon nanotubes on gold using a wet chemical self-assembling technique, *Langmuir* 16 (2000) 3569–3572.
- [11] M. Wilson, Paul FA., Growth of ionic crystals in carbon nanotubes, *J. Am. Chem. Soc.* 123 (2001) 2101–2102.
- [12] F. Akbal, Adsorption of basic dyes from aqueous solution onto pumice powder, *J. Colloid Interface Sci.* 286 (2005) 455–458.
- [13] D. Ugarte, A. Chatelain, W.A. Deherr, Nanocapillarity and chemistry in carbon nanotubes, *Science* 274 (1996) 1897–1901.
- [14] S.C. Tsang, Y.K. Chen, P.J.F. Harris, M.L.H. Green, A simple chemical method of opening and filling carbon nanotubes, *Nature* 372 (1994) 159–161.
- [15] T. Hyeon, S.S. Lee, J. Park, Y. Chung, H.B. Na, Synthesis of highly crystalline and monodisperse maghemite nanocrystallites without a size-selection process, *J. Am. Chem. Soc.* 123 (2001) 12798–12801.
- [16] C. Pascal, J.L. Pascal, F. Favier, Electrochemical synthesis for the control of gamma-Fe₂O₃ nanoparticle size, morphology, microstructure, and magnetic behavior, *Chem. Mater.* 11 (1999) 141–147.
- [17] J. Liu, A.G. Rinzler, H.J. Dai, J.H. Hafner, R.K. Bradley, P.J. Boul, A. Lu, Fullerene pipes, *Science* 280 (1998) 1253–1256.
- [18] P.K. Malik, Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36, *Dyes Pigments* 56 (2003) 239–249.
- [19] C. Namasivayam, R. Jayakumar, R.T. Yamuna, Dye removal from wastewater by adsorption on waste Fe (III)/Cr (III) hydroxide, *Waste Manage* 14 (1994) 643–650.