CHEMICAL ENGINEERING JOURNAL

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Simultaneous adsorption of atrazine and Cu (II) from wastewater by magnetic multi-walled carbon nanotube

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HIGHLIGHTS

▶ Magnetic carbon nanotubes were used to adsorb atrazine and Cu (II) simultaneously.
▶ The adsorbent exhibited good adsorption behavior for atrazine and Cu (II).
▶ Convenient magnetic separation and effective reuse.

ARTICLE INFO

ABSTRACT

In this paper, a magnetic multi-walled carbon nanotube (MMWCNT) was developed and investigated to explore the possible application in the simultaneous removal of atrazine and Cu (II) from contaminated water. The Brunauer–Emmett–Teller (BET) specific surface area, magnetization measurement, scanning electron microscopy (SEM), Thermo-gravimetric Analysis (TGA) and X-ray photoelectron spectroscopy (XPS) analyses were used to characterize the adsorbent. Batch adsorption experiments were conducted to study the sorption performance of MMWCNT. The adsorption of atrazine and Cu (II) were both unfavorable under acidic conditions. The sorption kinetics data were well described by pseudo-second-order kinetic model. The sorption isotherms for atrazine and Cu (II) were better fitted by Freundlich model and Langmuir model, respectively. Cu (II) had a strong suppression effect on atrazine uptake in the simultaneous adsorption and atrazine preloading experiment. As for Cu (II) preloading, the impact of atrazine on Cu (II) desorption was almost negligible. The regeneration of MMWCNT for several cycles using acidic ethanol solution and practical application of MMWCNT were also investigated. Due to its high adsorption capacity, easy separation and effective reusability, MMWCNT showed great potential in wastewater treatment.

1. Introduction

According to the layers involved, carbon nanotubes (CNTs) mainly include single-walled (SWCNTs) and multi-walled (MWCNTs) carbon nanotubes [1]. CNTs as novel adsorbents have attracted increasing attention of numerous researchers because of their large specific surface areas and unique structures. Extensive investigations for removal of contaminants, such as PAHs [2], naphthalene [3], microcystins [4], natural organic matter [5], cadmium [6] and zinc [7], suggest that CNTs exhibit high sorption capacities for various toxic organic compounds and metallic ions. However, CNTs suffer from separation inconvenience. Combining the magnetic properties of iron oxide with adsorption properties of CNTs is of increasingly environmental concern as a rapid, effective and promising technology for removing hazardous pollutants in water [8,9] and has been proposed for widespread environmental applications in wastewater treatment and potentially in situ remediation [10–12].

To date, several studies have reported the cosorption of metallic cations and organic compounds by CNTs and revealed that metal ions may affect the environmental fate of toxic chemicals or vice versa [13–16]. Also, recently, many research have been focused on employing various modified CNTs to better remove pollutants from wastewater [17–20]. However, very few reports have been

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cited in terms of utilizing magnetic CNTs to simultaneously adsorb heavy metal ions and organic contaminants.

Atrazine, a model selective triazine herbicide, has extensively been used to control broad-leafed weeds and grasses in crop production [21], and has frequently been detected in waters due to its long half-life, apparent mobility, moderate water solubility, great leaching potential and high chemical stability in soils and aquifers [22], leading to great ecological and human health concern. Some studies suggested that atrazine interferes with endocrine hormone metabolism [23] and may cause human liver cancer [24]. European countries have forbidden its application now and set a severe concentration limit of 0.1 ppb for atrazine in drinking water and the United States Environmental Protection Agency has also set a maximum contaminant level at 3 ppb for it [25]. Copper, one of the most widespread heavy metals in the environment, has universally been considered to be very toxic at high concentration. It can cause copper poisoning in humans such as gastrointestinal problems, kidney damage, hair loss, nausea, anemia, hypoglycemia, severe headaches and even death [26]. Although China issued the maximum acceptable concentration of copper in drinking water as $1.0 \, \mathrm{mg \, L^{-1}}$, Cu (II) commonly exists far above the limit in wastewater of copper plating, pharmaceuticals, minings, paints and especially pesticides [27,28] which poses a great threat to the ecological environment and human health. In this connection, it should be noted that there is a high possibility that atrazine and Cu (II) could occur together in mixed contaminant systems and the coexistence of them tend to influence their adsorption and fates in the environment. However, it lacks investigation on simultaneous removal of atrazine and Cu (II) by MMWCNT.

The objective of this work is to explore the possibility to produce MMWCNT as adsorbent for the removal of atrazine and Cu (II) from aqueous solution at the same time. The atrazine and Cu (II) adsorption kinetics and isotherms on MMWCNT, as well as the effect of Cu (II) on the sorption of atrazine and vice versa, were also investigated.

2. Materials and methods

2.1. Materials

MWCNT (>95%) with outer diameter 10–20 nm and length 10–30 μm was purchased from Chengdu Organic Chemistry Co. Ltd., Chinese Academy of Sciences. Atrazine (98.8%) was purchased from Sigma–Aldrich Chemical Co. and used directly as received. $Cu(NO_3)_2 \cdot 3H_2O$ and all other chemicals were of analytical grade. Tap water was derived from Changsha Running-water Company, China. River water was taken from Xiangjiang River, China. Preliminary experiments indicated that tap water and river water contained no detectable levels of atrazine or Cu (II).

2.2. Preparation of adsorbents

The preparation of MMWCNT was accomplished according to the previous literature [8,9] with some modification. Typically, 1.0 g MWCNT was suspended in 200 mL of mixed solution containing 1.7 g $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ and 2.51 g $NH_4Fe(SO_4)_2 \cdot 12H_2O$. Subsequently, 10 mL of 8 M NH_4OH solution was added dropwise to precipitate iron oxides with the aid of ultrasonic stirring for 10 min. The final mixture was adjusted to pH 11 and then allowed to react for 45 min at 250 rpm. All the above processes were maintained at 50 °C under high purity nitrogen atmosphere. After the reaction, the suspension was allowed to cool at room temperature. The product MMWCNT was separated from the mixture by a magnet and then washed five times with ultrapure water and absolute

alcohol, respectively, followed by overnight drying at 60 °C in a vacuum oven. Then, the obtained sample was put in a desiccator for further use. The magnetic iron oxides were directly prepared without adding MWCNT.

2.3. Characterization methods

The morphology and size analyses were performed by SEM using a JSM-5600 LV microscope (JEO, Ltd., Japan). The BET surface area was determined by ASAP 2020 Accelerated Surface Area and Porosimetry System (Micromeritics Instrument Corporation, USA). The surface elemental composition analyses were proposed based on the XPS spectra (Thermo Fisher Scientific, UK) with a resolution of 0.5 eV. The magnetization measurement was carried out using a vibrating sample magnetometer (VSM). The zeta potential of MMWCNT was recorded by a Zeta Meter 3.0 (Zeta Meter Inc.) equipped with a microprocessor unit. TGA was performed by a ZRY-2P thermal analyzer (China) in the temperature range of 20–800 °C at a heating rate of 20 °C/min.

2.4. Adsorption experiments

Batch adsorption experiments were conducted in 100-mL conical flasks in a shaker at 150 rpm at 25 ± 1 °C. The pH values of the solutions were adjusted with 0.1 M NaOH or 0.1 M HCl using a pH meter. $0.2 \, \mathrm{g \, L^{-1}}$ MMWCNT was used when the adsorption capacity was great both for atrazine and Cu (II) (Fig. S1).

2.4.1. Effect of solution pH

The flasks containing 50 mL of $5 \, \mathrm{mg \, L^{-1}}$ atrazine (or $30 \, \mathrm{mg \, L^{-1}}$ Cu (II)) and $0.2 \, \mathrm{g \, L^{-1}}$ MMWCNT were shaken for 24 h at different pH values ranging from 3.00 to 9.00. Subsequently, the adsorbents were separated followed by the analysis of residual atrazine (or Cu (II)) concentrations in supernatant.

2.4.2. Adsorption kinetics

The effect of contact time on the adsorption of atrazine (or Cu (II)) by MMWCNT, MWCNT and magnetic iron oxides were studied in flasks containing 50 mL of $5 \, \mathrm{mg \, L^{-1}}$ atrazine (or $30 \, \mathrm{mg \, L^{-1}}$ Cu (II)) and $0.2 \, \mathrm{g \, L^{-1}}$ MMWCNT at pH 6.0. The samples were taken from different flasks using pipette at predetermined time intervals (from 5 min to 24 h) and the remaining atrazine (or Cu (II)) concentrations in supernatant were determined.

To illustrate the adsorption process and provide insights into possible reaction mechanisms, a pseudo-second-order kinetic model was used to fit the experimental data, which can be expressed as

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{1}$$

where k $(\mathrm{g \, mg^{-1} \, h^{-1}})$ is the pseudo-second-order rate constant, q_t $(\mathrm{mg \, g^{-1}})$ and q_e $(\mathrm{mg \, g^{-1}})$ are the adsorbed amount of adsorbate at any time and at equilibrium, respectively.

2.4.3. Adsorption isotherms

The sorption isotherms experiments were performed in flasks containing 50 mL of $0.2 \, \mathrm{g \, L^{-1}}$ of MMWCNT and initial concentrations of atrazine varying from $1 \, \mathrm{mg \, L^{-1}}$ to $20 \, \mathrm{mg \, L^{-1}}$ or Cu (II) varying from $10 \, \mathrm{mg \, L^{-1}}$ to $100 \, \mathrm{mg \, L^{-1}}$ at pH 6.0 for 24 h.

Langmuir and Freundlich sorption isotherm models were used to determine the proper isotherm for atrazine and Cu (II) adsorption on MMWCNT. The equations of the Langmuir and Freundlich models can be expressed as

$$\mathrm{Langmuir}: q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

Freundlich $: q_e = K_F C_e^{1/n}$ (3)

where q_e (mg g^{-1}) is the adsorbed value of adsorbate at equilibrium, q_m (mg g^{-1}) is the maximum adsorption capacity, C_e (mg L^{-1}) is the equilibrium solute concentration, K_L (L mg^{-1}) is the Langmuir constant related to adsorption energy, K_F and n are Freundlich constants and intensity factors, respectively.

2.4.4. Competitive adsorption studies

Competitive adsorption experiments were operated when both adsorbates were adsorbed onto MMWCNT simultaneously or one of them was preloaded onto MMWCNT. In the simultaneous adsorption studies, the concentration of Cu (II) was fixed at 30 mg L^{-1} (or atrazine 5 mg L^{-1}) while the concentration of atrazine (or Cu (II)) varied. In the preloading studies, Cu (II) (or atrazine) was first adsorbed onto MMWCNT and then the Cu (II) (or atrazine)-adsorbed MMWCNT were added into different concentrations of atrazine (or Cu (II)) solutions for further adsorption. The above tests were all carried out in flasks containing 50 mL of 0.2 g L^{-1} of MMWCNT at 150 rpm at 25 ± 1 °C at pH 6.0. After 24 h, the adsorbents were separated and the remaining Cu (II) (or atrazine) concentrations in supernatant were analyzed.

2.5. Desorption and regeneration studies

The feasibility of regenerating MMWCNT for repeated use was investigated by using acidic ethanol solution. Basically, batch equilibrium tests were first performed in flasks containing 50 mL of 5 mg L^{-1} atrazine (or 30 mg L^{-1} Cu (II)) and 0.2 g L^{-1} MMWCNT at 150 rpm at 25 ± 1 °C at pH 6.0 for 24 h. Then MMWCNT were magnetically separated and the supernatant was accordingly analyzed. Subsequently, the atrazine-adsorbed (or Cu (II)-adsorbed) adsorbents were added into 50 mL of 20% (volume ratio) ethanol at pH 3.0 for desorption at 150 rpm at 25 ± 1 °C for 24 h. After the regenerated MMWCNT was recycled, the concentration of atrazine (or Cu (II)) in supernatant was determined.

2.6. Application of MMWCNT to real water samples

The tests were performed in flasks containing 50 mL of 0.2 g L^{-1} MMWCNT and 5 mg L^{-1} or 10 mg L^{-1} atrazine (30 mg L^{-1} or 50 mg L^{-1} Cu (II)) at 150 rpm at 25 ± 1 °C for 24 h. The atrazine and Cu (II) stock solution were prepared using tap water and river water. The pH of these solutions was not adjusted to study the effect of real conditions.

2.7. Analysis

All adsorption experiments were conducted in triplicate. After reaction, the MMWCNT was separated from the solutions using a magnet. Atrazine concentrations in the supernatants were determined by HPLC (Agilent 1100, USA) equipped with an UV–vis photodiode array detector while Cu (II) concentrations were determined by a Perkin-Elmer Analyst 700 atomic absorption spectrophotometer (AAS, Perkin-Elmer, USA). The amount of adsorbed atrazine or Cu (II) was determined by the difference between initial and final equilibrium concentrations.

3. Results and discussion

3.1. Characterization

Fig. 1 shows the morphologies and sizes of MWCNT, iron oxides and MMWCNT. It was observed that MWCNT had a diameter of
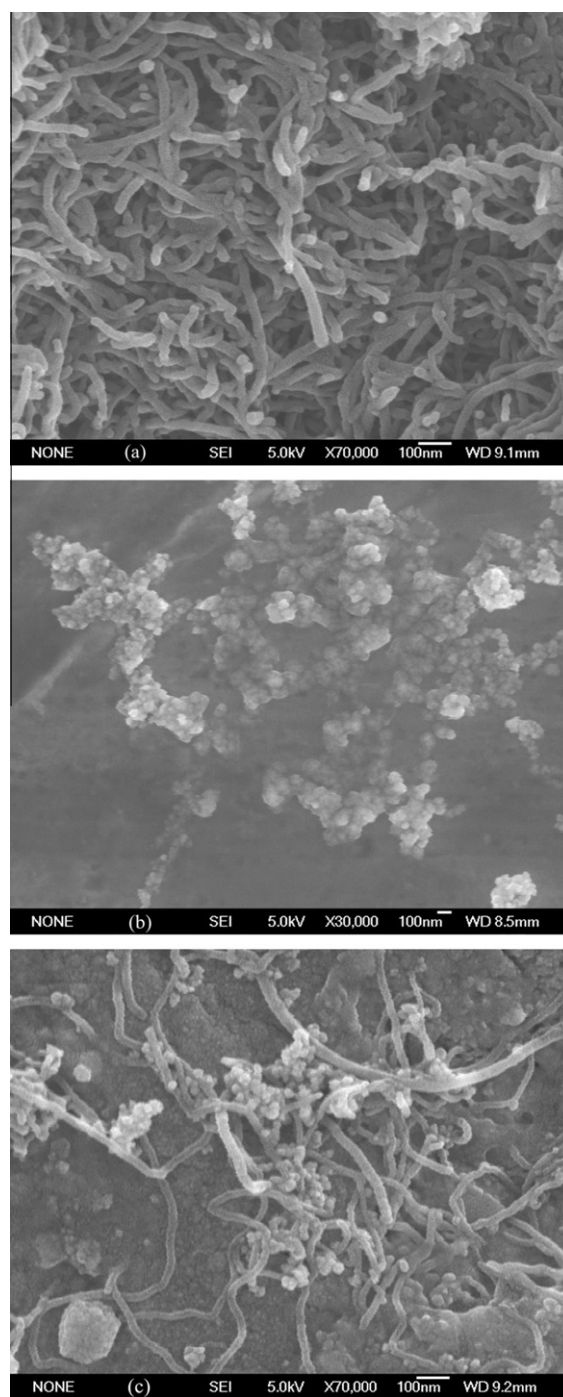

Fig. 1. SEM images of MWCNT (a), iron oxides (b) and MMWCNT (c).

about 36 nm and a tubular structure with crosslinks (Fig. 1a). Iron oxides had a diameter of about 100 nm and congregated together closely (Fig. 1b). Fig. 1c indicates that iron oxides were successfully loaded on the surface of MWCNT to produce MMWCNT and their size were smaller than that presented in Fig. 1b.

Based on the previous XRD work [9], it was expected that four types of iron oxides were formed in the MMWCNT including magnetite (Fe$_3$O$_4$), maghemite (γ-Fe$_2$O$_3$), hematite (α-Fe$_2$O$_3$) and goethite (FeO(OH)). Among them, only magnetite and maghemite are magnetic.

The iron oxides content of MMWCNT was evaluated using TGA. It was observed that the weight of iron oxides remained almost un-
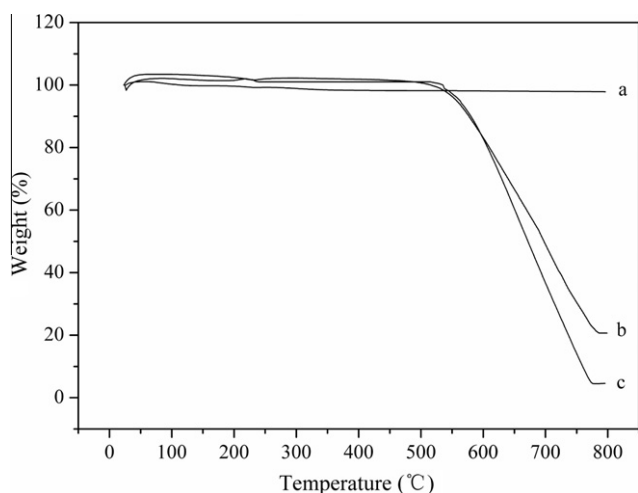
Fig. 2. TGA curves of iron oxides (a), MMWCNT (b) and MWCNT (c).

changed (Fig. 2a). The TGA curve of MWCNT (Fig. 2c) shows an obvious weight loss over the range of 550–760 °C which was caused by the oxidization of the nanotubes [29,30] and the MWCNT could be burned almost completely. For MMWCNT (Fig. 2b), about 20 wt% of residual yield was found. Therefore, the percent of iron oxides in the MMWCNT should be around 20% [29,30].

The BET measurements revealed that the specific surface areas (SSA) of MWCNT and MMWCNT were 162.99 $m^2 g^{-1}$ and 138.66 $m^2 g^{-1}$, respectively, from which it could be concluded that the SSA of MWCNT was larger than that of the same weight of iron oxides loaded onto MMWCNT. The saturated magnetization of MMWCNT is 8.06 emu g^{-1} (displayed in Fig. 3), which is sufficient enough to be separated from aqueous solution using high density magnet compared with the saturated magnetization values (6.1 emu g^{-1} and 2.5 emu g^{-1}) reported in previous studies [31,32].

Fig. 4 presents the XPS spectra of MMWCNT, atrazine-adsorbed MMWCNT and Cu (II)-adsorbed MMWCNT. Compared with the XPS spectra of MMWCNT (Fig. 4a), a N 1s peak (Fig. 4b) as an indicator of atrazine sorption and a Cu 2p peak (Fig. 4c) as an indicator of Cu (II) sorption on MMWCNT were detected at the binding energy of 399.55 eV and 933.79 eV, respectively, which provided the evidence that both atrazine and Cu (II) were indeed adsorbed onto MMWCNT.
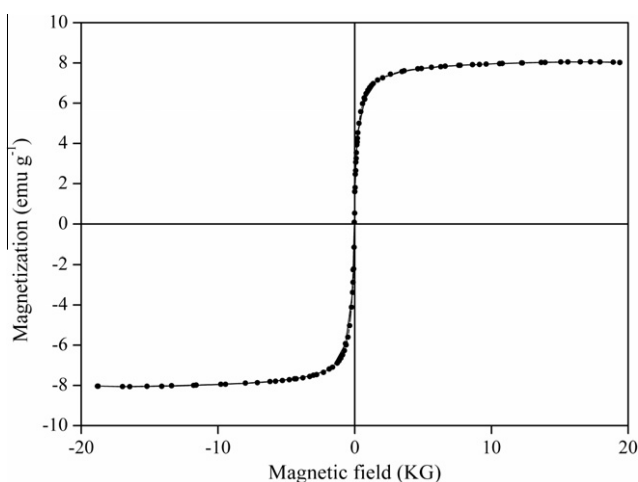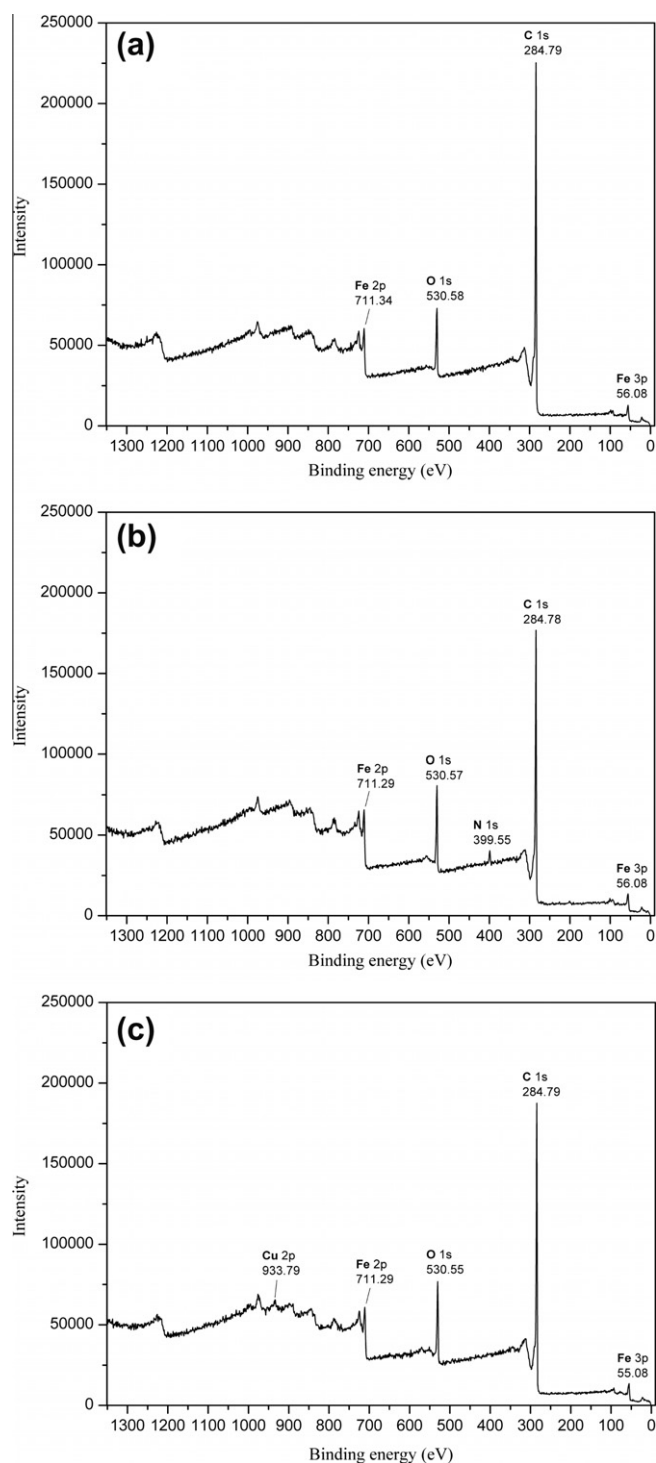

Fig. 3. Magnetization curve of MMWCNT.

Fig. 4. XPS spectra of MMWCNT (a), atrazine-adsorbed MMWCNT (b) and Cu (II)-adsorbed MMWCNT (c).

3.2. Effect of pH

The effect of pH on the adsorption of atrazine was illustrated in Fig. 5a. It was found that the adsorbed amount of atrazine by MMWCNT was the lowest at pH 3.0 but remained almost constant above pH 3.0 (4.0–9.0). Atrazine is a weak base, with a pK_a of 1.7. When pH is near its pK_a, half of atrazine is present in the cationic form while the other half stays in the non-ionic form. An increasing pH could result in a decreasing cationic fraction of atrazine in solu-
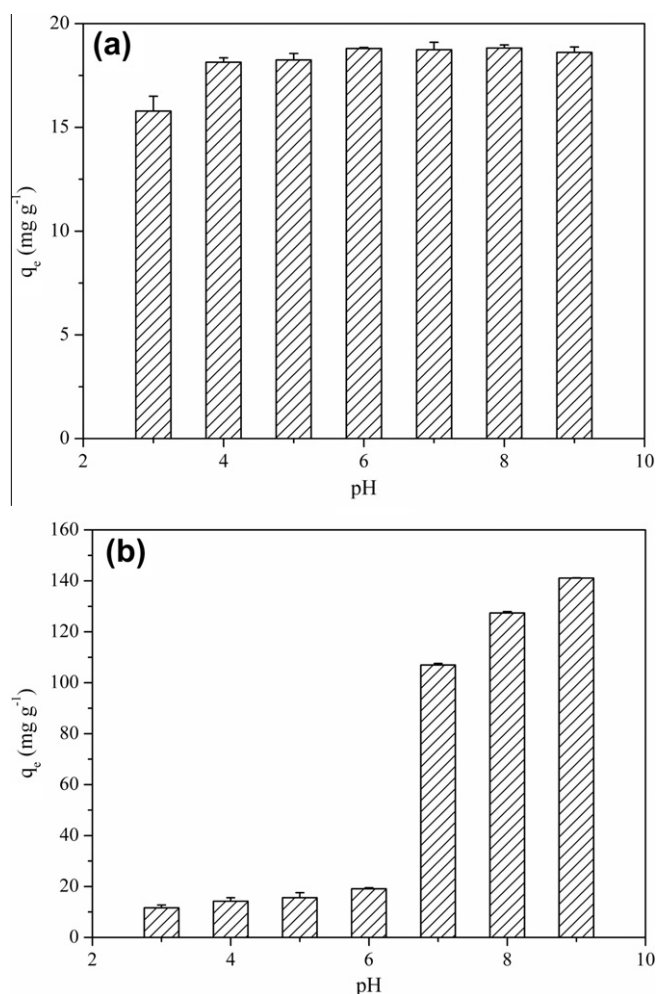
Fig. 5. Effect of pH on the adsorption of atrazine (a) and Cu (II) (b) by MMWCNT.

Fig. 6. Zeta potentials of MMWCNT at various pH values.
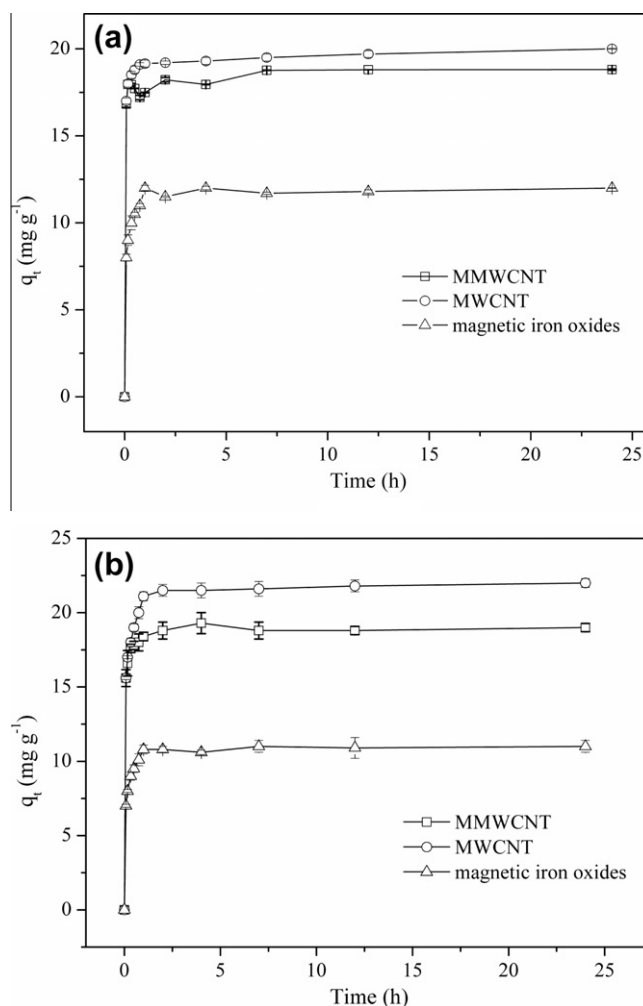
Fig. 7. Effect of contact time on the adsorbed amount of atrazine (a) and Cu (II) (b) by MMWCNT, MWCNT and iron oxides.

tion. At pH 3.0 where atrazine is protonized and MMWCNT is positively charged (see Fig. 6), the electrostatic repulsion between atrazine and MMWCNT makes atrazine adsorption unfavorable. At higher pH (4.0–9.0), atrazine exists almost exclusively as neutral molecules [33] and weak forces such as van der Waals forces, hydrogen bonds and hydrophobic interactions would involve in the reciprocity of atrazine with MMWCNT and similar results have been reported by Chen et al. [13] for the adsorption of atrazine on MWCNTs.

The effect of pH on the adsorption of Cu (II) was shown in Fig. 5b. It was noted that the adsorption capacity for Cu (II) increased slightly over the pH range of 3.0–6.0 but increased rapidly over the range of 6.0–9.0. The result could be explained by electrostatic forces. Noticeably, the zeta potential of MMWCNT decreased as pH increased and the isoelectric point of MMWCNT was about 5.2 (depicted in Fig. 6). Consequently, the negatively charged MMWCNT (pH > 5.2) resulted in the electrostatic attraction favorable to Cu (II) adsorption by MMWCNT, whereas the positively charged MMWCNT (pH < 5.2) had an adverse effect. Over the pH range of 6.0–9.0, the removal efficiency increased significantly because of the combined role of adsorption and precipitation. However, the precipitation was dominated [14,34,35].

3.3. Adsorption kinetics

The effect of contact time on the adsorption of atrazine by MMWCNT, MWCNT and magnetic iron oxides was displayed in

Fig. 7a. It was found that as for MMWCNT, the adsorption rate increased dramatically within 10 min as the adsorbed amount of atrazine reached 17.95 mg g^{-1} when the initial atrazine concentration was 5 mg L^{-1}. Subsequently, a slight fluctuation occurred during the next several hours and apparent equilibrium was achieved

at about 7 h. The rapid uptake revealed that there was a strong adsorption affinity between atrazine and MMWCNT mainly owing to a large SSA (138.66 $m^2 g^{-1}$) of the adsorbent, while the slight fluctuation indicated that the second step (particle diffusion) in the adsorption was occurring so that atrazine molecules traveled within the pores of MMWCNT excluding a small amount of adsorption which took place on the exterior surface of the adsorbent [36], resulting in a relatively long time to reach the equilibrium.

The adsorption kinetic behavior of MMWCNT toward Cu (II) was described in Fig. 7b. It was observed that the sorption process was very fast during the first 20 min followed by a slow increase before the equilibrium was reached at about 6 h. In addition to the large SSA, the negative charge and functional groups on MMWCNT also facilitated the adsorption of Cu (II) due to electrostatic attraction and chelating formation [13], respectively.

Fig. 7 also shows that the adsorption ability of MWCNT for both atrazine and Cu (II) was a little greater than that of MMWCNT while the adsorption ability of iron oxides was much lower than that of MMWCNT. The BET measurements revealed that the specific surface areas (SSA) of MWCNT and MMWCNT are 162.99 $m^2 g^{-1}$ and 138.66 $m^2 g^{-1}$, respectively. The larger SSA contributed to better adsorption performance of MWCNT. However, MWCNT suffered from separation inconvenience. The low adsorption capacity of magnetic iron oxides for both atrazine and Cu (II) was mainly due to its poor dispersing performance (Fig. 1b) and small SSA [37]. MMWCNT not only had relatively high adsorption capacity, but also could be easily separated from aqueous solution by using magnet, which made it a promising adsorbent in the application of wastewater treatment.

The adsorption of atrazine and Cu (II) on MMWCNT was mainly physical force while the chemisorption played a small role due to a few oxygen-containing functional groups on MWCNT. Both chemisorption and particle diffusion contributed to the rate-controlling step [36,38].

Table 1 shows a linear relationship with very high correlation coefficients (R^2) between t/q_t and t for both atrazine and Cu (II), indicating that the adsorption processes of atrazine and Cu (II) by MMWCNT followed the pseudo-second-order kinetic model quite well.

3.4. Adsorption isotherms

The corresponding values of Freundlich and Langmuir isotherms were listed in Table 2. Comparisons of the experimental data and model fits of the two isotherms for atrazine and Cu (II) were presented in Fig. 8.

Table 1
Kinetic parameters for atrazine and Cu (II) adsorption by MMWCNT, modeled by pseudo-second-order model.

Adsorbate	k	$q_{e,measured}$	$q_{e,calculated}$	R^2
Atrazine	1.007	18.80	18.83	0.9999
Cu (II)	1.851	19.00	18.98	1.000

Table 2
Langmuir and Freundlich parameters for atrazine and Cu (II) adsorption by MMWCNT.

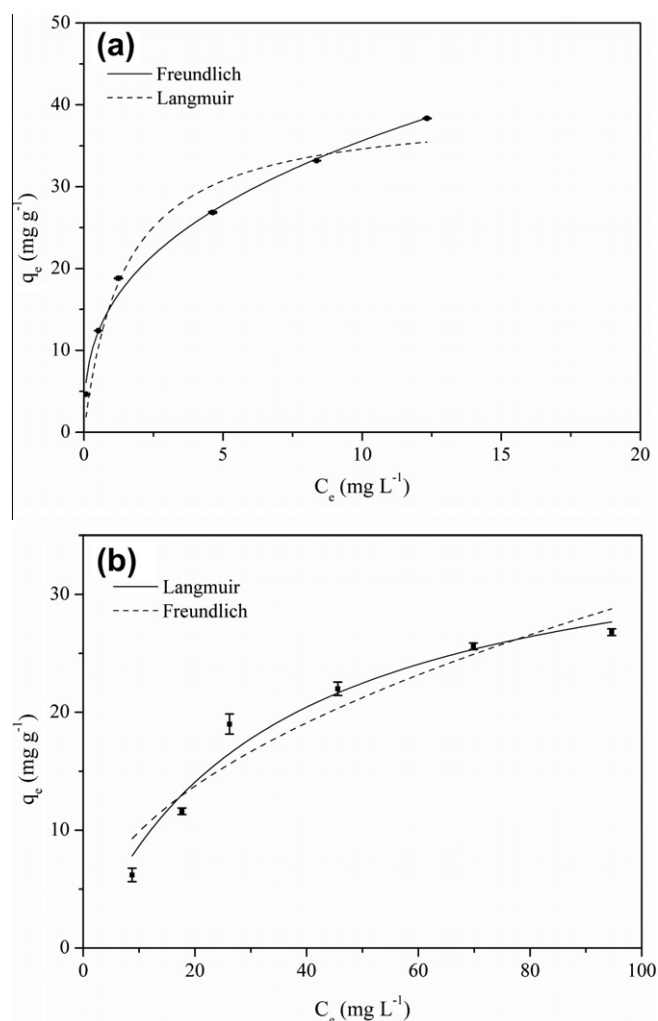|	Langmuir			Freundlich		
	K_L	q_m	R^2	K_F	n	R^2
Atrazine	0.7710	40.16	0.9800	14.87	2.505	0.9900
Cu (II)	0.02610	38.91	0.9600	1.987	1.644	0.9100

Fig. 8. Comparison of the experimental data and model fits of the Langmuir and Freundlich isotherms for the adsorption of atrazine (a) and Cu (II) (b) by MMWCNT.

It was observed that the Freundlich isotherm better described the adsorption of atrazine with the higher correlation coefficient R^2, suggesting that some heterogeneity on the surfaces or pores of MMWCNT played an important role in atrazine adsorption and different sites with several adsorption energies were involved. The results were consistent with the previous works where the Freundlich isotherm was more suitable than the Langmuir isotherm for the adsorption of atrazine on various adsorbents, such as conventional and surface modified activated carbons [39], Nyex 100 [40], humic acid–silica gel mixtures [41], sewage sludge-amended luvisol soil [42] and humic acids coated nanoparticles [43]. Value of $1/n < 1.0$ represents an advantageous adsorption condition. Therefore, the Freundlich exponent $1/n$ gave an indication of the favorability of atrazine adsorption by MMWCNT.

However, adsorption data for Cu (II) were better fitted with the Langmuir isotherm (see Table 2 and Fig. 8b), from which it could be assumed that the adsorbed Cu (II) formed monolayer coverage on the adsorbent surface and all adsorption sites were equal with uniform adsorption energies without any interaction between the adsorbed molecules. Similar results have also been observed by earlier researchers [44–47]. In order to determine the favorability of Cu (II) adsorption process, a dimensionless constant (R_L) called separation factor or equilibrium parameter was given according to Eq. (4) [48].

$$R_L = \frac{1}{1 + K_L C_0} \qquad (4)$$

where K_L (L mg^{-1}) is the Langmuir constant and C_0 (mg L^{-1}) is the initial Cu (II) concentration. The value of R_L indicates the type of the isotherm to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). All the R_L values lay between 0 and 1, signifying that the adsorption of Cu (II) onto MMWCNT was favorable. Moreover, the R_L values decreased as the initial Cu (II) concentration increased, suggesting that the adsorption process was more favorable at higher initial concentrations.

3.5. Comparison with other adsorbents

The sorption capacities of atrazine and Cu (II) on MMWCNT were compared with MWCNT itself and other adsorbents previously reported in the literature. It was noticed that MWCNT had a little higher removal efficiency for both atrazine and Cu (II) in our experiments (Fig. 7), which could be attributed to its relatively larger SSA. Despite this, a major advantage of being effectively and conveniently separated from solution and considerably higher uptake capacity than many other adsorbents made MMWCNT a promising and excellent adsorbent to remove atrazine and Cu (II) simultaneously in terms of potential application in wastewater treatment. The q_m value for atrazine (40.16 mg g^{-1}) was preponderant when compared with adsorbents such as zeolite X (11.86 mg g^{-1}) [49], heat-treated kerolite (15.2 mg g^{-1}) [50], activated carbon/iron oxide (22 mg g^{-1}) [21], MWCNTs-O (7.07%) (24.04 mg g^{-1}) [51] and SMWNT20 (31.37 mg g^{-1}) [52]. As for Cu (II), the q_m value (38.91 mg g^{-1}) was much higher than that of adsorbents such as tannic acid-immobilized activated carbon (2.23 mg g^{-1}) [53], carboxymethylated-bacterial cellulose (12.63 mg g^{-1}) [54], collagen-tannin resin (17.02 mg g^{-1}) [55] and was comparable to that of hydroxy quinoline immobilized bentonite (32.17 mg g^{-1}) [56], natural clay (44.84 mg g^{-1}) [57], pectin-iron oxide magnetic nanocomposite (48.99 mg g^{-1}) [35]..

3.6. Competitive adsorption between atrazine and Cu (II)

Competitive adsorption of atrazine and Cu (II) was evaluated when both adsorbates were adsorbed simultaneously and atrazine was preloaded on MMWCNT (Fig. 9). In the simultaneous adsorption studies, the higher Cu (II) concentration was, the less

adsorption capacity for atrazine became, which suggested that Cu (II) had a suppression effect on the atrazine sorption. Two mechanisms might be involved in this fact. On the one hand, direct competition for certain adsorption sites on MMWCNT occurred between Cu (II) and atrazine. On the other hand, the formation of inner-sphere and outer-sphere complexes of Cu (II) through carboxylic groups and hydration on the surfaces of MMWCNT and the existence of large and compact metal cation hydration shells on metal chelates indirectly competed with atrazine for sorption sites through squeezing, occupying and shielding part of the MMWCNT hydrophilic and hydrophobic sites [13,58]. Correspondingly, for atrazine-preloading experiments, more atrazine were desorbed in higher concentration of Cu (II) solution, which again showed that Cu (II) could compete with atrazine for the same adsorption sites. Since atrazine adsorption was better fitted by the Freundlich isotherm indicative of diverse sites with different adsorption energies, the weakly-adsorbed atrazine were desorbed and replaced by Cu (II) and with the more Cu (II) coexisting, the more pressure atrazine would be confronted with.

The effects of simultaneous adsorption experiments by fixing Cu (II) concentration but varying atrazine concentrations, and by preloading MMWCNT with Cu (II) followed by exposure to different concentrations of atrazine solution were also investigated (Fig. 9). In the simultaneous adsorption studies, atrazine with different concentrations had a relatively smaller suppression effect on the sorption of Cu (II) while in the Cu (II)-preloading experiments, few Cu (II) were desorbed. The above two phenomenon could be explained by a stronger affinity between Cu (II) and MMWCNT due to electrostatic attraction at pH 6.0 and the steric hindrance effect of the formation of inner-sphere and outer-sphere complexes of Cu (II) on the surfaces of MMWCNT, respectively.

3.7. Regeneration of MMWCNT

There was smaller adsorption capacity at lower pH values for both adsorbates and high solubility in ethanol for atrazine. Additionally, better desorption behavior occurred in 20% acidic ethanol (Table S1). Therefore, the feasibility of regenerating MMWCNT was evaluated using 20% acidic ethanol solution at pH 3.0. Table S2 showed the stability of MMWCNT in acidic ethanol solution since the adsorption ability of MMWCNT as well as the magnetism were almost not affected. Fig. 10 indicated that there were still high adsorption capacities for both atrazine and Cu (II) in the fourth cycle (70% for atrazine and 88% for Cu (II) compared with the initial
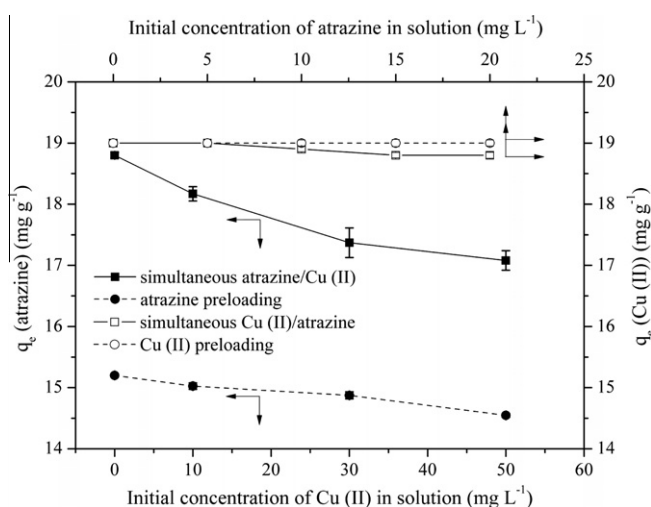

Fig. 9. Effects of simultaneous adsorption and atrazine (Cu (II)) preloading on the sorption capacity of MMWCNT for atrazine (Cu (II)). The fixed concentration of atrazine and Cu (II) was 5 mg L^{-1} and 30 mg L^{-1}, respectively.
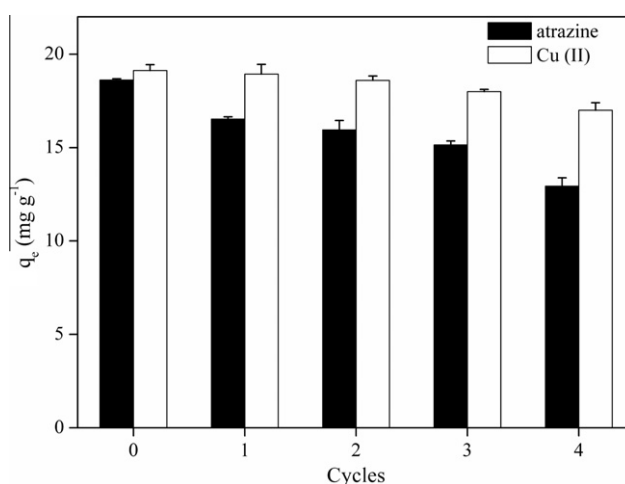

Fig. 10. Adsorption–desorption cycles of MMWCNT for atrazine and Cu (II).

Table 3
The practical application of MMWCNT to real samples (tap water and river water).

Adsorbate	Initial concentration in solution (mg L^{-1})	q_e (mg g^{-1})		
		Ultrapure water (pH 6.0)	Tap water (pH 7.1)	River water (pH 7.8)
Atrazine	5	18.80	18.68	21.02
	10	26.86	26.85	30.25
Cu (II)	30	19.00	139.20	130.00
	50	22.00	175.00	162.20

cycle) although the removal efficiency declined with the cycles, which demonstrating that MMWCNT could be regenerated effectively by ethanol with high acidity and thus be reused repeatedly.

3.8. Application of MMWCNT to real water samples

MMWCNT was used to treat real samples including tap water and river water to investigate its practical application. The corresponding results were listed in Table 3. It was found that the adsorption capacity for atrazine in tap water was almost equal to that in ultrapure water while the adsorption capacity for atrazine in river water was a little greater than that in ultrapure water. Fig. 5a showed that the adsorbed amount of atrazine by MMWCNT remained almost constant over the pH range of 6.0–9.0 and thus pH would not affect the adsorption performance. In river water, better removal performance might be due to the presence of dissolved organic matter, such as humic acid and fulvic acid [41,43,59]. As for Cu (II), the adsorption capacity in tap water and river water both greatly increased compared to that in ultrapure water. This could be explained by the combined role of adsorption of MMWCNT and precipitation of Cu (II) (Fig. 5b). Also, Fig. 6 showed that higher pH was favorable to Cu (II) adsorption due to electrostatic attraction. These results indicated that MMWCNT exhibited good behavior in removing atrazine or Cu (II) in real samples.

4. Conclusions

Magnetic multi-walled carbon nanotubes combining properties of carbon nanotubes and magnetism were synthesized for the simultaneous removal of atrazine and Cu (II). The SEM characterization provided the evidence that iron oxides were successfully loaded onto MMWCNT while the XPS analyses demonstrated that atrazine and Cu (II) were indeed adsorbed onto MMWCNT. Both of the adsorption of atrazine and Cu (II) by MMWCNT were fast and fitted the pseudo-second-order kinetic model very well. The Freundlich isotherm gave a superior fit for atrazine. But for Cu (II), the Langmuir isotherm was better modeled. The maximum adsorption capacity of MMWCNT for atrazine and Cu (II) were 40.16 mg g^{-1} and 38.91 mg g^{-1}, respectively. Competitive adsorption experiments showed that MMWCNT had a preferential binding capacity for Cu (II). The desorption studies revealed that MMWCNT could be effectively regenerated by ethanol with high acidity. The practical application investigation indicated that MMWCNT exhibited good behavior in removing atrazine or Cu (II) in real samples. In conclusion, MMWCNT may be a suitable candidate in environmental protection owing to its high adsorption capacity for atrazine and Cu (II) as well as convenient magnetic separation.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2012.09.102.

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