

# Three-Dimensional Electro-Fenton Degradation of Methyleneblue Based on the Composite Particle Electrodes of Carbon Nanotubes and Nano-Fe<sub>3</sub>O<sub>4</sub>

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**Abstract** Carbon nanotubes/magnetic nano-Fe<sub>3</sub>O<sub>4</sub> composite (CNTs/Fe<sub>3</sub>O<sub>4</sub>NPs) were prepared by chemical coprecipitation. Ti/SnO<sub>2</sub> electrode was used as the anode, the CNTs/Fe<sub>3</sub>O<sub>4</sub> composite as particle electrodes, and graphite electrode as cathode respectively. Four different systems for degradation of methylene blue (MB) in neutral medium were investigated: Ti/SnO<sub>2</sub> anode (A), Ti/SnO<sub>2</sub> anode with CNTs particle electrodes (B), Ti/SnO<sub>2</sub> anode with Fe<sub>3</sub>O<sub>4</sub>NPs particle electrodes (C), and Ti/SnO<sub>2</sub> anode with CNTs/Fe<sub>3</sub>O<sub>4</sub>NPs particle electrodes (D). It was found that D system exhibited much higher MB degradation efficiency than others, attaining 82 % in 30 min. The enhanced efficiency was attributed to Ti/SnO<sub>2</sub> anodic direct oxidation of MB and CNTs/Fe<sub>3</sub>O<sub>4</sub> NPs composite particle electrodes which could activate molecule oxygen to produce more H<sub>2</sub>O<sub>2</sub> and ·OH. CNTs/Fe<sub>3</sub>O<sub>4</sub> NPs particle electrodes could achieve magnetic separation easily for reuse and exhibited good degradation efficiency to MB.

**Keywords** CNTs/ Fe<sub>3</sub>O<sub>4</sub> NPs · 3D-E-Fenton · Degradation of methyleneblue

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## الخلاصة

تم توليف مركب أنابيب الكربون النانوية/أكسيد الحديد (الماجنتايت) النانوي (CNTs/Fe<sub>3</sub>O<sub>4</sub> NPs) عن طريق الترسيب المشترك. وقد استخدم إلكترود التيتانيوم/أكسيد القصدير كقطب سالب (أنود)، ومركب CNTs/Fe<sub>3</sub>O<sub>4</sub> كإلكترودات جسيمات وإلكترود الجرافيت كقطب سالب (كاثود)، على التوالي. وتم التحقيق في أربعة نظم مختلفة لتكسير الميثيلين الأزرق (MB) في وسط متعادل هي: (أ) أنود التيتانيوم/أكسيد القصدير، (ب) أنود التيتانيوم/أكسيد القصدير مع إلكترودات جسيمات أنابيب الكربون النانوية، (ج) أنود التيتانيوم/أكسيد القصدير مع إلكترودات جسيمات الحديد النانوية و (د) أنود التيتانيوم/أكسيد القصدير مع إلكترودات جسيمات أنابيب الكربون النانوية /أكسيد الحديد النانوية. ووجد أن نظام د يظهر كفاءة تكسير للميثيلين الأزرق أعلى من النظم الأخرى بالحصول على كفاءة من 82% في 30 دقيقة. وتعزى الكفاءة المعززة إلى التأكسد المباشر الأنودي بالتيتانيوم/أكسيد القصدير للميثيلين الأزرق وإلى إلكترودات جسيم مركب أنابيب الكربون النانوية/أكسيد الحديد (الماجنتايت) النانوي الذي يمكنه أن ينشط الأكسجين الجزيئي لكي ينتج البيروكسайд وأيون الهيدروكسي. ويمكن لإلكترودات جسيم مركب أنابيب الكربون النانوية/أكسيد الحديد (الماجنتايت) النانوي أن تحقق فصلا مغناطيسيا سهلا من أجل إعادة استخدام كفاءة تكسر جيدة للميثيلين الأزرق وإظهارها.

## 1 Introduction

Water pollution caused by toxic and nonbiodegradable organic materials brings about very serious health threats. Recently, advanced oxidation processes (AOPs) for wastewater treatment have attracted more attention because of their formation of hydroxyl radicals (·OH). Hydroxyl radicals is one of the most powerful oxidizing species in aqueous environment. Among the AOPs, the E-Fenton systems can continuously supply H<sub>2</sub>O<sub>2</sub> through the two-electron reduction of oxygen, which has proven to be one of the most effective methods to degrade organic pollutants in wastewater. However, there are some drawbacks in this classic homogeneous E-Fenton system. First, the ferric ions left in the wastewater require a separation step. Sec-

ond, classic E-Fenton's reagents work well only within a narrow pH range (pH 3–4) because of iron precipitates at higher pH values. Third, the high cost of Fe anode makes it impractical for its large-scale application in wastewater treatment. Therefore, researchers have taken great efforts to solve these problems. One effort is to develop a E-Fenton-like system containing other transition metals [1]. Another effort is to develop heterogeneous three-dimensional electrode system [2] containing solid phase catalysts. For example, goethite, hematite, clay minerals, iron hydroxide and iron loaded on silica or on alumina were used previously. The third effort is to develop a stable titanium-based anode, such as Ti/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>5</sub>, and Ti/Co/SnO<sub>2</sub> to accelerate the generation of hydroxyl radicals [3].

In the heterogeneous three-dimensional electrode system, carbon blacks were frequently used as the carrier for electrocatalysts due to its high surface area. Compared with carbon blacks, carbon nanotubes (CNTs) has the characteristics of high electrical conductivities, good absorption, good electrocatalyse effect, and good corrosion resistance especially under the highly oxidizing conditions, and has attracted more and more attention as cathode for electrochemical oxidation [4–6]. But less attention has been paid to CNTs as the three-dimensional electrode for H<sub>2</sub>O<sub>2</sub> electro-generation [7], although CNTs have good electrical conductivity and mechanical strength, relative chemical inertness to most electrolyte solutions, high surface activity, as well as a wide operational potential window [8].

In this paper, methylene blue was used as model contaminant, CNTs/Fe<sub>3</sub>O<sub>4</sub> as a novel particle electrode were synthesized in order to improve the classical E-Fenton system. Meanwhile Ti/SnO<sub>2</sub> was used as anode since it can directly generate hydroxyl radicals [9]. Combination 3D-E-Fenton system of CNTs/Fe<sub>3</sub>O<sub>4</sub> particle electrode with Ti/SnO<sub>2</sub> anode was expected to increase current efficiency and degradation efficiency of methylene blue. The result suggested that this 3D-E-Fenton system can attain good degradation efficacy with methylene blue. Besides this system could work at a near neutral medium, and CNTs/Fe<sub>3</sub>O<sub>4</sub> particle electrode could be easily separated by magnetic field without losing activity after long-term run.

## 2 Experimental Sections

### 2.1 Chemicals

Carbon nanotubes (CNT; >95 % purity; diameter, 20–30 nm; length, 1–5 μm) were purchased from Shenzhen Nanotech Co. Ltd.(Shenzhen, China). Titanium plates were purchased from New State Titanium metal (Xi'an, China). Methyleneblue (MB) were purchased from Tianjin Lidong Reagent

Factory. Tin(IV)chloride pentahydrate (SnCl<sub>4</sub>·5H<sub>2</sub>O) were purchased Sinopharm Chemical Reagent Co., Ltd, Other chemical reagents were analytical grade. Distilled water was used.

### 2.2 Preparation of CNTs/nano-Fe<sub>3</sub>O<sub>4</sub> Composite

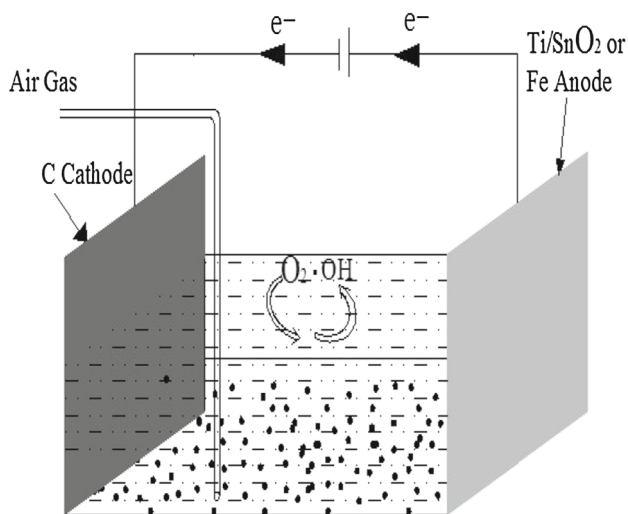
Further purification of the carbon nanotubes was performed by refluxing the CNT in concentrated nitric acid at 60 °C for 12 h. The obtained CNT was dried at 105 °C for 4 h. The CNT/Fe<sub>3</sub>O<sub>4</sub> nanoparticle composite was prepared by chemical coprecipitation of Fe<sup>2+</sup> and Fe<sup>3+</sup> in alkaline solution in the presence of CNTs. The molar ratio of Fe<sup>2+</sup>:Fe<sup>3+</sup> was 1:2. The magnetic composite was prepared by suspending 1.0 g purified CNT in 200 mL of solution containing 1.99 g (10.0 mmol) FeCl<sub>2</sub>·H<sub>2</sub>O and 5.41 g (20.0 mmol) FeCl<sub>3</sub>·H<sub>2</sub>O. After the solution was sonicated (30 W, 40 kHz) for 10 min, NH<sub>4</sub>OH aqueous solution was added dropwise to precipitate the iron oxides while the mixture solution was sonicated. The pH of the final mixture should be in the range of 10–11. To promote the complete growth of the nanoparticle crystals, the reaction was carried out at 65 °C for 30 min under mechanical stirring. The precipitate was separated by the magnetic field, and washed with doubly distilled water and ethanol for three times respectively. Subsequently, the composite was dried under vacuum. The content of CNT in the composite was approximately 50 wt%. If no CNT was added to the coprecipitation solution of Fe<sup>2+</sup> and Fe<sup>3+</sup>, pure Fe<sub>3</sub>O<sub>4</sub> nanoparticles could be obtained [10].

### 2.3 Characterization of the Fe<sub>3</sub>O<sub>4</sub> Nanoparticle and the CNT/nano-Fe<sub>3</sub>O<sub>4</sub> Composite

X-ray powder diffraction (XRD) patterns were obtained on a X-ray diffractometer with Cu radiation (Japanese Rigaku, D/Max-3c). Transmission electron microscopy (TEM) study was carried out on electron microscopy instrument (Japanese electronics company, JEM-2100).

### 2.4 Preparation of Ti/SnO<sub>2</sub> Electrode

The Ti plates (6 × 3 × 0.1 cm) were used as substrates. First, Ti plates were polished with sandpaper, degreased in 40 % NaOH solution with sonicated treatment for 30 min, etched in a boiling 10 % oxalic acid solution for 1 h. Then, a solution containing 0.050 M SnCl<sub>4</sub> and 20 % citric acid monohydrate was dissolved in ethanol was used to electro-deposit Sn onto the Ti plates. The applied voltage was 1.5–2.5 V and the current was 10 mA/cm<sup>-2</sup> using DC stabilized power supply (HCP-03-150, Yangzhou Huatai). The modified Ti plates was dried in air. The process of electrodeposition was repeated for 5–6 times and the electrode were introduced in an oven at 550 °C for 2 h [11].



**Fig. 1** Schematic diagram of the electrochemical cell apparatus

Electrochemical measurements were performed on a CHI660 electrochemical workstation (Chenhua Instruments Co., Shanghai, China). The experiments were carried out using a conventional three-electrode system with an Ti or Ti/SnO<sub>2</sub> electrode as working electrode, a platinum wire as the counter electrode and an calomel electrode as the reference electrode. All potentials were referred to this reference electrode.

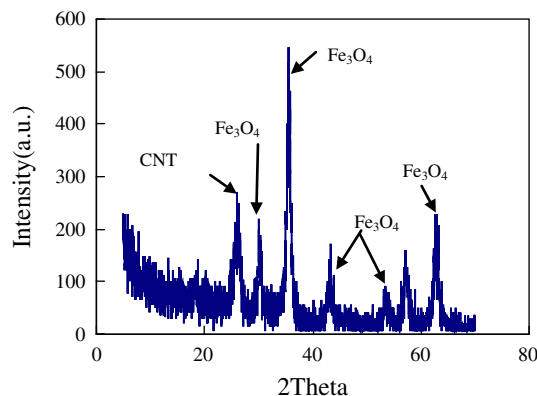
### 2.5 Degradation of MB and Analytical Methods

Degradation of MB by three-dimensional electrode processes was performed in a cell of 150 mL, as shown in Fig. 1. Ti/SnO<sub>2</sub> electrode was used as anode and immersion partial area of the anode was 3 × 3 cm. The graphite electrode was used as cathode. The space between the anode and the cathode was about 4–5 cm. DC voltage was applied. During the experiments, the voltage between the anode and the cathode was 5 V. The initial concentration of MB was 2.4 × 10<sup>-4</sup> M. 0.10 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> solution was used as supporting electrolyte in 150 mL, 10 g/L CNTs/Fe<sub>3</sub>O<sub>4</sub> as particle electrodes, dissolved oxygen by aeration. The solution was mechanically stirred and maintained at room temperature during the whole degradation reaction. A UV-visible spectrophotometer (TU-1901, Beijing Purkinje General instrument Co. Ltd) was used to monitor the concentration of MB in water at its maximum absorption wavelength of 650 nm.

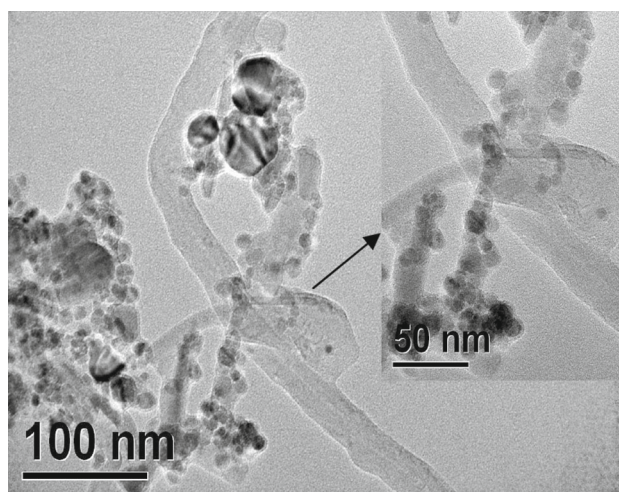
## 3 Results and Discussion

### 3.1 Characterization of the CNTs/Fe<sub>3</sub>O<sub>4</sub> Composite

The X-ray diffraction (XRD) patterns of the CNT/Fe<sub>3</sub>O<sub>4</sub> composite is shown in Fig. 2. It was found that the pattern



**Fig. 2** XRD patterns of the as-prepared CNTs/Fe<sub>3</sub>O<sub>4</sub>

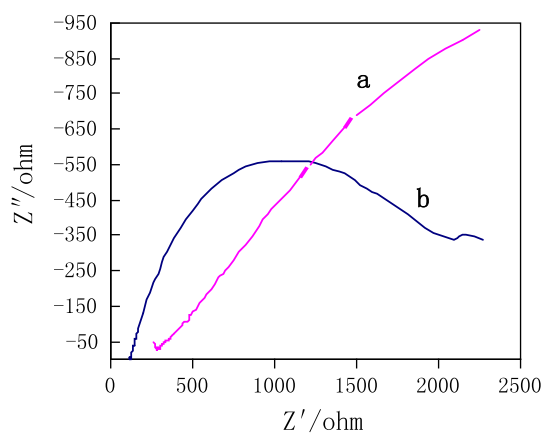


**Fig. 3** TEM image of the as-prepared CNTs/nano-Fe<sub>3</sub>O<sub>4</sub>

matched well with the standard Fe<sub>3</sub>O<sub>4</sub> patterns (JCPDS No. 65-3107) and the standard CNTs patterns (JCPDS, file No. 74-444) [12]. The diffraction peaks at 2θ value of 26.5° is ascribed to the reflection of the CNTs. The diffraction peaks at 2θ values of 30.2°, 35.6°, 43.3°, 54.1°, 57.3° and 63.8° can be assigned to the reflection of Fe<sub>3</sub>O<sub>4</sub> nanocubes. These XRD results suggested that Fe<sub>3</sub>O<sub>4</sub> successfully deposited on the CNTs. Figure 3 shows the TEM images of the prepared the CNT/Fe<sub>3</sub>O<sub>4</sub> composite. The result of TEM suggested that the Fe<sub>3</sub>O<sub>4</sub> are deposited on CNTs and the size distribution of Fe<sub>3</sub>O<sub>4</sub> was in the range 5–10 nm.

### 3.2 Electrochemical Characterization of the Ti/SnO<sub>2</sub> Electrode

The procedure in which SnO<sub>2</sub> electrochemically deposited on the surface of Ti was described in Sect. 2.4. In order to investigate the properties of the modified electrode, especially investigate the dynamics process of charge transfer and



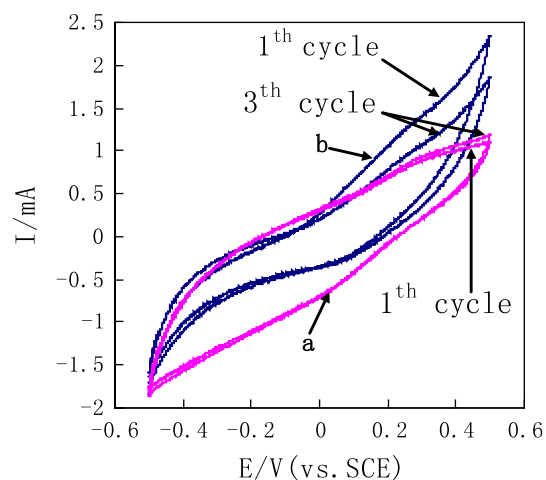
**Fig. 4** Nyquist plots of impedance spectra obtained in 5 mM  $K_3Fe(CN)_6$  solution at  $Ti/SnO_2$  anode (a) and bare Ti anode (b). The biased potential was 0.20 V. The frequency was from 100 kHz to 0.1 Hz and the amplitude was 5.0 mV

electron transfer between modified membrane/electrolyte interfaces, the Nyquist plots of impedance spectra were recorded to investigate the  $Ti/SnO_2$  electrode. The Nyquist plots of impedance spectra at different electrodes are shown in Fig. 4. Horizontal ordinate is the impedance real part  $Z'$  and vertical coordinates is imaginary part  $Z''$ . The bare Ti electrode exhibited very big semicircle at high frequencies, and the electron transfer resistance (Ret) is about 2000 (curve b). The  $Ti/SnO_2$  exhibited an almost straight line at high frequencies (curve a). In theory, the deposition of  $SnO_2$  on the surface of Ti can decrease the impedance of Ti electrodes [13, 14]. That is to say, the  $Ti/SnO_2$  electrode exhibited better electroconductibility than the Ti electrode. Thus the obtained return suggested that Sn was deposited on the surface of the Ti electrode.

Since cyclic voltammetry can be used to estimate the microcosmic reaction process of the electrode' surface, here this method was used to investigate the stability of the  $Ti/SnO_2$  electrode. The cyclic voltammograms of bare Ti electrode and  $Ti/SnO_2$  electrode is shown in Fig. 5. The cyclic voltammograms at bare Ti electrode (curve b) revealed the oxidation current of third cycle was decreased than first cycle. However, the cyclic voltammograms of  $Ti/SnO_2$  electrodes showed the current of third cycle and first cycle were almost unchanged (curve a). Moreover, with the scanning continuation, the oxidation current decreases gradually at Ti electrode. While with the scanning continuation, the oxidation current was almost invariable at  $Ti/SnO_2$  electrodes. The result indicated that  $Ti/SnO_2$  electrodes as anode had the better stability than the bare Ti electrodes.

### 3.3 Degradation of MB in the 3D-E-Fenton System

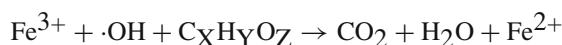
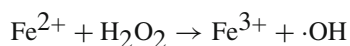
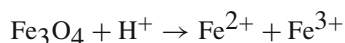
Degradation of MB in aqueous solution was used to test the efficiency of the 3D-E-Fenton system. Four different systems



**Fig. 5** Cyclic voltammograms of the  $Ti/SnO_2$  electrode (a) and Ti electrode (b) in 5 mM  $K_3Fe(CN)_6$  solution at neutral pH (vs SCE, scan rate of 0.10 V/s)

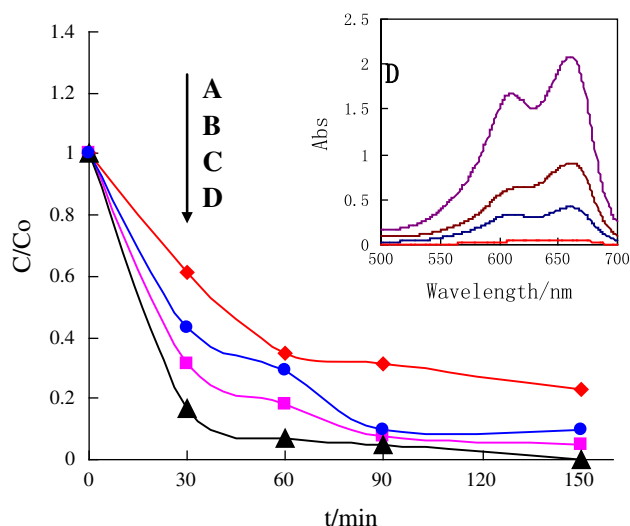
for degradation of MB in near neutral medium were investigated, which were  $Ti/SnO_2$  anode (A system),  $Ti/SnO_2$  anode with CNTs as particle electrodes (B system),  $Ti/SnO_2$  anode with  $Fe_3O_4$  NPs particle electrodes (C system), and  $Ti/SnO_2$  anode with CNTs/ $Fe_3O_4$  NPs particle electrodes (D system), as shown in Fig. 6. After 30 min of reaction, 82 % of MB was degraded in the D system, 75 % of MB was degraded in the C system, 67 % of MB was degraded in B system and only 40 % of MB was degraded in A system. Also, after 60 min, the degradation efficiency in the D system was the best. One reason is the added particle electrodes could adsorb MB, resulting in the higher degradation of MB in B, C, D system. In addition, the presence of CNTs in CNTs/ $Fe_3O_4$  not only increased current efficiency [15], but also provided iron source for the proceeding of the E-Fenton reaction. Here carbon nanotube can contribute to adsorb dissolved oxygen and improve charge transfer to produce more  $H_2O_2$  [7].

In our experiment, it was found that  $Fe_3O_4$  NPs could be slightly dissolved in weakly acid medium and even in neutral medium, forming  $Fe^{2+}$  ions and  $Fe^{3+}$  ions (the date was shown in the Supporting information).  $Fe^{2+}$  ions or  $Fe^{3+}$  ions can both react with  $H_2O_2$  to produce oxidizing agent  $\cdot OH$  as follows [16, 17].

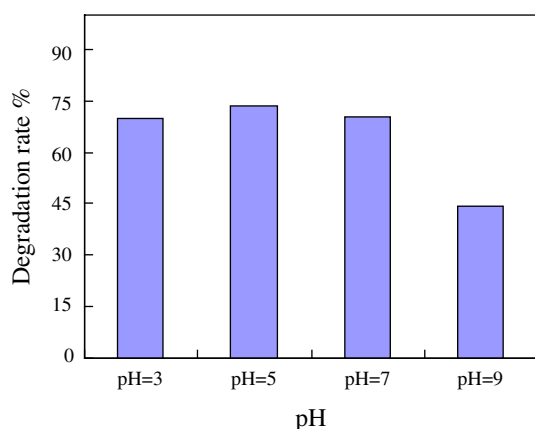


While after 150 min, although the degradation of MB in D system attained 97.8 %, it seems to have little difference between C and D after 150/90 min, meaning that the nanotubes make little contribution to the degradation. Therefore, the D system exhibited better degradation efficiency in





**Fig. 6** Degradation of MB in different systems Ti/SnO<sub>2</sub> anode (A), Ti/SnO<sub>2</sub> anode with CNTs as particle electrodes (B), Ti/SnO<sub>2</sub> anode with Fe<sub>3</sub>O<sub>4</sub> NPs particle electrodes (C), and Ti/SnO<sub>2</sub> anode with CNTs/Fe<sub>3</sub>O<sub>4</sub> NPs particle electrodes (D),  $2.4 \times 10^{-4}$  mol/L MB The inset is the UV-vis spectral changes of MB with reaction time at pH 5



**Fig. 7** The effect of pH on the degradation efficiency of MB in the 3D-E-Fenton system based on Ti/SnO<sub>2</sub> anode with CNTs/Fe<sub>3</sub>O<sub>4</sub> NPs particle electrodes for 30 min

a shorter time and it can be regarded that it has potential application in lowering the cost. The absorption spectra of procedure is recorded in inset of Fig. 6. In the 3D-E-Fenton systems, the regeneration of Fe<sup>2+</sup> can occur either by the oxidation with an organic radical, or by the reaction with H<sub>2</sub>O<sub>2</sub>. Compared with the classic Fenton systems, the 3D-E-Fenton systems can avoid the addition of expensive H<sub>2</sub>O<sub>2</sub> and maintain an almost constant concentration of electro-generated H<sub>2</sub>O<sub>2</sub> during the whole pollutants removal process. The CNTs/Fe<sub>3</sub>O<sub>4</sub> nanotubes could serve as an effective heterogeneous Fenton reagent to catalytic produce ·OH radicals and be easy to magnetic separate for reuse.

The influence of the initial pH on the degradation efficiency of this 3D-E-Fenton system was also investigated, as shown in Fig. 7. It was found that the catalytic ability of

the CNTs/Fe<sub>3</sub>O<sub>4</sub> NPs particle electrodes was affected by pH value. After 30 min of reaction, the degradation ratios corresponding to pH 7, pH 3, pH 5, and pH 9 were 70.5, 69.7, 73.6 and 44.2 % respectively. There were no obvious differences for degradation of MB in neutral and acid medium. Thus this 3D E-Fenton system can work well within a wide pH range compared with classic Fenton's reagents. One report indicates that the near CNT surface pH is at least two units lower than the bulk pH [5]. That is the reason for better degradation of MB when pH was 5. CNTs could activate molecule oxygen to simultaneously electrochemically reduce oxygen into hydrogen peroxide because of high electrical conductivities, and good absorption with gas. In addition, ions (Fe<sup>3+</sup> or Fe<sup>2+</sup>) would be partially dissolved from CNTs/Fe<sub>3</sub>O<sub>4</sub> NPs particle electrodes which could react with H<sub>2</sub>O<sub>2</sub> producing ·OH radicals effectively.

## 4 Conclusion

In summary, a composite CNTs/Fe<sub>3</sub>O<sub>4</sub> was prepared by chemical co-precipitation. The Ti/SnO<sub>2</sub> anode by cathodic electrodeposition method was fabricated. A novel 3D-E-Fenton system with the composite CNTs/Fe<sub>3</sub>O<sub>4</sub> as particle electrodes and Ti/SnO<sub>2</sub> as anode has been developed to degrade MB. The 3D-E-Fenton system could efficiently degrade of MB in 30 min; the degradation efficiency of MB can attain 82 % at pH 5.

Cyclic voltammetric and impedance spectra experiment revealed that Ti/SnO<sub>2</sub> anode had low impedance and good stability after long-term run. CNTs could activate molecule oxygen to simultaneously electrochemically reduce oxygen into hydrogen peroxide and Fe<sub>3</sub>O<sub>4</sub> could catalyze hydrogen peroxide into hydroxyl radical. These two Fenton reagents further reacted together to produce hydroxyl radicals. The 3D-E-Fenton system is expected to have potential application in waste water treatment due to its excellent degradation efficiency, stability of CNTs/Fe<sub>3</sub>O<sub>4</sub> NPs, repeat utilization and no secondary pollution.

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## References

1. Ai, Z.; Xiao, H.; Mei, T.: Electro-fenton degradation of rhodamine B based on a composite cathode of Cu<sub>2</sub>O nanocubes and carbon Nanotubes. *J. Phys. Chem. C.* **112**, 11929–11935 (2008)
2. Mo, D.-Q.; Guo, Y.-D.: Treatment of rhodamine B wastewater by three-dimensional electrode reactor with hydrogen peroxide. *Environ. Sci. Technol.* **34**(6), 167–172 (2011)
3. Ma, C.; Tan, F.; Zhao, H.; Chen, S.; Quan, X.: Sensitive amperometric determination of chemical oxygen demand using Ti/Sb-

- SnO<sub>2</sub>/PbO<sub>2</sub> composite electrode. *Sens. Actuators B*. **155**, 114–119 (2011)
- Ghaedi, M.; Ghobadzadeh, P.; Kokhdan, S.N.; Soyak, M.: Oxidized multiwalled carbon nanotubes as adsorbents for kinetic and equilibrium study of removal of 5-(4-dimethyl amino benzylidene) rhodanine. *Arab. J. Sci. Eng.* **38**, 1691–1699 (2013)
  - Gao, G.; Vecitis, C.D.: Electrochemical carbon nanotube filter oxidative performance as function of surface chemistry. *Environ. Sci. Technol.* **45**, 9726–9734 (2011)
  - Wu, Y.; Chen, L.; Xie, K.; Li, J.; Chen, Y.: Synthesis and characterization of multi-wall carbon nanotubes supported-hydrated iron phosphate cathode material for lithium-ion cells by a novel homogeneous precipitation method. *Ionics* **18**, 721–729 (2012)
  - Briyyo, P.J.; Santhanam, K.S.V.; Rabio, A.; Alonso, J.A.; Ajayan, P.M.: Improved charge transfer at carbon nanotube electrodes. *Adv. Mater.* **11**, 2–4(1999)
  - Sljukic, B.; Banks, C.E.; Compton, R.G.: Iron oxide particles are the active sites for hydrogen peroxide sensing at multiwalled carbon nanotube modified electrodes. *Nano Lett.* **6**, 1556–1558 (2006)
  - Wang, F.; Yany, X.; Xua, M.; Li, S.; Fang, W.: Electrochemical performance and electroreduction of maleic acid on Ce-doped nano-TiO<sub>2</sub> film electrode. *Electrochim. Acta.* **97**, 253–258 (2013)
  - Qu, S.; Wang, J.; Kong, J.; Yang, P.; Chen, G.: Magnetic loading of carbon nanotube/nano-Fe<sub>3</sub>O<sub>4</sub> composite for electrochemical sensing. *Talanta* **71**, 1096–1102 (2007)
  - Zhenhai, L.; Rongpeng, W.; Caimei, F.: Preparation and characterization of cerium doped Ti/SnO<sub>2</sub>-Mn<sub>2</sub>O<sub>3</sub>/PbO<sub>2</sub> electrode. *J. Rare Earth.* **25**(1), 91–96 (2007)
  - Meng, J.; Yang, G.; Yan, L.; Wang, X.: Synthesis and characterization of magnetic nanometer pigment Fe<sub>3</sub>O<sub>4</sub>. *Dyes Pigm.* **66**(2), 109–113 (2005)
  - Li, X.; Shen, L.; Zhang, D.; Qi, H.; Gao, Q.; Ma, F.; Zhang, C.: Electrochemical impedance spectroscopy for study of aptamer-thrombin interfacial interactions. *Biosens. Bioelectron.* **23**, 1624–1630 (2008)
  - Lisdat, F.; Schäfer, D.: The use of electrochemical impedance spectroscopy for biosensing. *Anal. Bioanal. Chem.* **391**, 1555–1567 (2008)
  - Andriiko, A.A.; Globa, N.I.; Zul'figarov, A.O.; Prisiazhnyi, V.D.; Sementsov, Ju.I.; Potaskalov, V.A.: Discharge-ionization of hydrogen on modified carbonnanotube electrodes. *Int. J. Hydrogen Energy* **38**, 5983–5988 (2013)
  - Li, J.; Ai, Z.; Zhang, L.: Design of a neutral electro-Fenton system with Fe@Fe<sub>2</sub>O<sub>3</sub>/ACF composite cathode for wastewater treatment. *J. Hazard. Mater.* **164**, 18–25 (2009)
  - Isarain-Chávez, E.; Cabot, P.L.; Centellas, F.; Rodríguez, R.M.; Arias, C.; Garrido, J.A.; Brillas, E.: Electro-Fenton and photoelectro-Fenton degradations of the drug beta-blocker propranolol using a Pt anode: Identification and evolution of oxidation products. *J. Hazard. Mater.* **185**, 1228–1235 (2011)

