



Intensified internal electrolysis for degradation of methylene blue as model compound induced by a novel hybrid material: Multi-walled carbon nanotubes immobilized on zero-valent iron plates (Fe⁰-CNTs)

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HIGHLIGHTS

- ▶ A Fe⁰-CNTs hybrid plate was produced as technical improvement for micro-electrolysis.
- ▶ The oxidative pretreatment of carbon nanotubes enhanced the reactivity of Fe⁰-CNTs.
- ▶ The Fenton-like oxidation pathway was verified to play the major role on degradation.
- ▶ The stoichiometrical relation between H⁺ and DO control the reaction pathway.

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ABSTRACT

This paper reported a novel iron–carbon hybrid material (Fe⁰-CNTs) as a technical improvement of internal electrolysis for water treatment. This material was fabricated by means of electrophoresis deposition (EPD) to immobilize carbon nanotubes on the surface of zero-valent iron plate and then stabilized by calcinations. The reactivity of Fe⁰-CNTs was examined by the degradation kinetics of methylene blue (MB) used as model compound. The presence of Fe⁰-CNTs material in water induced considerable enhancement in reaction rates, which was attributed to the numerous microscopic iron–carbon galvanic cells formed in situ. The oxidative pretreatment of carbon nano-tubes largely facilitated the electrochemical process due to the improvement in surface chemistry. The thickness of CNTs layer was optimized at about 10 μm (EPD time of 3 min) for a better performance of Fe⁰-CNTs. The Fenton-like oxidation chain reactions following Reactions (1)–(3) was verified to play the key role on the degradation of target organics. The direction of this pathway has been analyzed to depend on a complex stoichiometrical relation between hydrogen ion (H⁺) and dissolved oxygen (DO), since side reactions may also take place consuming both of them. This functionalized Fe⁰-CNTs material working through micro-electrolysis exhibited appreciable advantages in terms of reactivity, durability and operational simplicity. The knowledge gained from the effect of solution environments is of importance for process control.

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1. Introduction

Zero-valent iron (ZVI), as a robust reducing agent or electron donor, can spontaneously initiate a series of chain reactions in water which are usually called the internal electrolysis (IE) or micro-electrolysis [1–4]. This abundant and nontoxic metal has been intensively employed in researches for the remediation of aqueous environment, including groundwater purification [5], biodegrad-

ability enhancement for produced water [6], decolorization [7], heavy metal removal [8] and wastewater detoxification of anthropogenic chemicals such as DDT [9] and atrazine [10]. In order to improve the efficiency of IE driven by ZVI, dispersive carbon particles, serving as active cathodes or facilitators, are commonly used in combination with iron chips [11–13] to form a lot of local batteries in multiphase mixtures, and reactions involving chemical decomposition of organics are believed to occur on or adjacent to carbon surface. Carbon nano-tubes are in one of the smallest carbon-organized tubular structures of long, thin, hollow cylinder, and their unique combination of physical and chemical property has drawn a great deal of interest and concern [14–17]. Owing to

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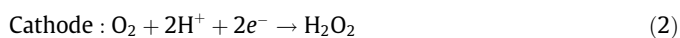
some of the advantages including high electro-conductivity [15] and larger mesoporous area, carbon nano-tubes have been considered as a promising alternative material to promote the efficiency of IE, if, they were introduced as the cathode.

The traditional dispersive IE systems suffer the limitations of mass transfer since the electron delivery from iron to carbon requires first contact or collision between these solid “electrodes”, though great efforts have been paid in order to remedy this defect by complementary means of ultrasonic agitation [11] or others. Iron oxides or hydroxide precipitates would be generated in the process of IE on the surface of iron forming an inhibitory coating that covers the metallic iron core, which often lead to the diminution of reactivity [18]. For the mixed iron/carbon multiphase reactor, additional operation steps are needed on the separation of solid loadings from the liquid phase after reactions. These drawbacks inspired the idea to design a kind of combined iron-carbon material with high effectiveness and operational feasibility. Taking into consideration the carbon nano-tubes in diameters usually no more than 100 nm, it is possible to realize the extensive immobilization of them on the surface of iron to form a hybrid structure with numerous microscopic galvanic cells in place of the macroscopic ones in iron/carbon dispersions. Thus the deliberate preparation of such a functionalized integrative material is expectable.

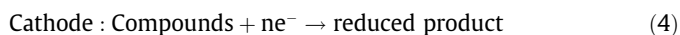
In IE process, anodic Fe^0 serves as an active electron donor ($E^0(\text{Fe}^{2+}/\text{Fe}^0) = -0.44 \text{ V}$):



As to the mechanism of reactions taking place on the cathodes, two governing pathways have been reported to date, i.e. the mediate Fenton-like oxidation [19] and reduction [20]. The first one can be expressed by a sequential chain reactions accompanied by the generation of H_2O_2 ($E^0(\text{H}_2\text{O}_2/\text{H}_2\text{O}) = +1.349 \text{ V}$ [21]) which will quickly be decomposed by ferrous ions (Fe^{2+}) to produce high oxidative hydroxyl radicals (HO^\cdot ; $E^0 = +2.80 \text{ V}$ [22]) following the well-known Fenton process. This set of chain reactions has been suggested by Shimizu et al. [23] through the detection of HO^\cdot in a lately published literature.



The functional pathways induced by IE for the removal of contaminants are not a matter of consensus since reductive contribution has also been indicated, as van der Zee et al. [24] reported the reductive decomposition of azo dye on the surface of carbon acting as a redox mediator or terminal electron acceptor which can be described in Reaction (4). Yang [12] proposed another way in which the hydrogen ions (H^+) was first reduced into hydrogen (H_2) by accepting electrons shown in Reaction (5), and then the freshly formed hydrogen drove the reductions in cathodic region.



The Fenton-like chain reactions (Reactions (1)–(3)), among all the possible electrochemical actions, can offer highly oxidative HO^\cdot radicals capable in dealing with a variety of organic substances. For this reason, it has been believed as the desired pathway in the process of IE for environmental practice. In contrast to the relative abundant supplement of Fe^{2+} , the dissociative hydrogen ions (H^+) and dissolved oxygen (DO) are thought to be key or controlling factors for the direction of Reaction (2). The solution pH has been suggested to affect the reduction kinetics in some cases [11,25]. DO is the particular parameter never taking part in the reductions, but probably plays an important role on advanced

oxidation. Chen et al. [26] documented that the aerobic experiment with oxygen pumping attained much higher TOC abatement compared with anaerobic conditions without oxygen. It has also been mentioned that dissolved oxygen would be consumed following different ways depending on the supplement of H^+ [27]. To our knowledge, the detailed effect of DO on reaction kinetics was seldom reported. The collective investigation on the impact of pH and DO seems necessary for the mechanism study as well as for better process control.

The phenothiazines form a large class of basic drugs widely used for the treatment of mental disorders, antihistamines and antidyskinetics [28]. Owing to their diverse pharmacological actions and widespread applications, a considerable amount of phenothiazines used for pharmaceutical preparations have been discharged into environment. With strong antibacterial nature, wastewaters containing phenothiazines or the analogues may pose an obstacle to biological treatment. We choose methylene blue (MB) as the model compound in this work for one reason that it has extensive pharmacological utilization [29] as phenothiazine derivative. In addition to this, it can be fast detected by UV-Vis method to obtain more detailed information on degradation kinetics due to its light-sensitive nature (662 nm for monomer, 610 nm for dimer and 292 nm for phenothiazine structure [30]).

In this paper, we reported a novel Fe^0 -CNTs hybrid material which was prepared through chemical immobilization of oxidized carbon nanotubes (CNTs) onto the surface of zero-valent iron plate (Fe^0). The objectives of this study are: (i) to examine the reactivity of Fe^0 -CNTs for its potential application; (ii) to evaluate the effect of preparation factors on the performance of Fe^0 -CNTs including the pretreatment of CNTs and time of electrophoresis deposition; (iii) to investigate the effect of pH and DO on reaction kinetics for process control.

2. Materials and methods

2.1. Materials

Multi-walled carbon nanotubes (diameter 60–100 nm, length 5–15 μm , purity > 97%) were purchased from Shenzhen Nanotech Port. Co. (China). To remove organic/inorganic impurities, they were heated at 350 $^\circ\text{C}$ for 30 min and purified with hydrochloride (HCl) according to Datsyuk et al. [31]. Then the obtained carbon nanotubes were designated as pristine sample and labeled as “CNTs,p”. In the process of oxidative pretreatment, pristine carbon nanotubes were immersed into concentrated mixture of nitric acid/sulfuric acid at 1:3 (v/v). Then the mixture was stirred at least 19 h to ensure a full contact, refluxed by distilled water to neutral, filtered to form a solid bulk with cracks and dried overnight at 150 $^\circ\text{C}$. Subsequently, the prepared solid was milled by agate mortar and stored in a drying bottle. The oxidized carbon nanotubes were labeled as “CNTs” and used throughout this work.

Zero-valent iron plates (labeled as Fe^0) were used as substrates (length \times width \times thickness = 4 cm \times 4 cm \times 1 mm) and its metal compositions are listed in Table 1. They were first burnished by fine abrasive-papers, and then chemically polished by dipping into hydrofluoric acid/hydrochloric acid/distilled water mixtures (v/v/v = 1:3:3) to remove the impurities and iron oxides on the surface.

Table 1
Metal composition of Fe^0 used as the substrate in this study.

Element	wt.%
Fe	99.5909
Mn	0.2672
Al	0.0392
Cr	0.0183

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