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Microwave-induced carbon nanotubes catalytic degradation of organic pollutants in aqueous solution

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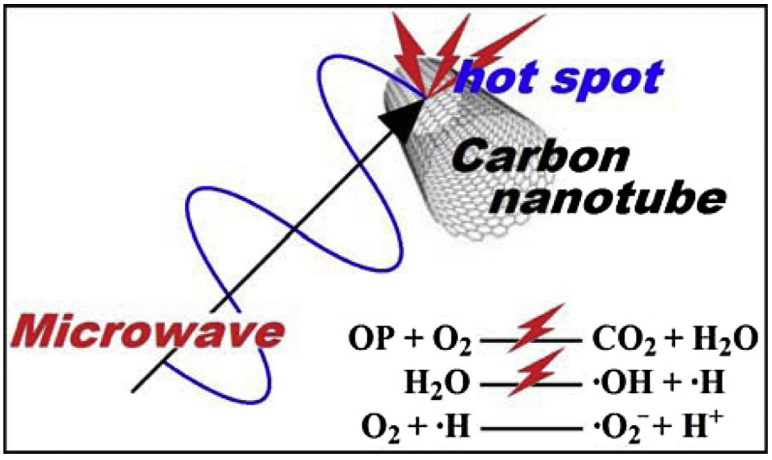
HIGHLIGHTS

- Microwave-induced CNTs-based catalytic degradation technology is developed.
- Microwave catalytic activities of CNTs with different diameters are compared.
- Organic pollutants with different structure can be degraded in MW/CNTs system.
- The 10–20 nm CNTs shows the higher catalytic activity under MW irradiation.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a new catalytic degradation technology using microwave induced carbon nanotubes (MW/CNTs) was proposed and applied in the treatment of organic pollutants in aqueous solution. The catalytic activity of three CNTs of 10–20 nm, 20–40 nm, and 40–60 nm diameters were compared. The results showed that organic pollutants such as methyl orange (MO), methyl parathion (MP), sodium dodecyl benzene sulfonate (SDBS), bisphenol A (BPA), and methylene blue (MB) in aqueous solution could be degraded effectively and rapidly in MW/CNTs system. CNTs with diameter of 10–20 nm exhibited the highest catalytic activity of the three CNTs under MW irradiation. Further, complete degradation was obtained using 10–20 nm CNTs within 7.0 min irradiation when 25 mL MO solution (25 mg/L), 1.2 g/L catalyst dose, 450 W, 2450 MHz, and pH = 6.0 were applied. The rate constants (k) for the degradation of SDBS, MB, MP, MO and BPA using 10–20 nm CNTs/MW system were 0.726, 0.679, 0.463, 0.334 and 0.168 min^{-1}, respectively. Therefore, this technology may have potential application for the treatment of targeted organic pollutants in wastewaters.

1. Introduction

In the manufacture of various industrial products, a large number of hazardous organic pollutants are discharged into aquatic

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systems without any effective treatment, which can endanger aquatic life and harm human health [1–5]. In the reported technologies for the removal of toxic organic pollutants, some non-destructive methods can only transfer organic pollutants from one phase to another phase, easily causing secondary pollution [6]. Also, some oxidation technologies, including advanced oxidation processes (AOPs), usually need significantly long treatment time before complete mineralization and incomplete degradation sometimes occurs during the stepwise oxidation processes [7–10]. Therefore, it is urgent and of critical importance to develop new rapid and cost-effective treatment technologies for the complete degradation of organic pollutants in wastewater.

In recent years, microwave (MW) technology has been exploited as a powerful tool in treating organic pollutant wastewater. The application is based on the rapid, efficient, and selective heating properties of MW [11]. When a MW-absorbing material, such as activated carbon (AC) with large surface area and different pore size distributions, is used under MW irradiation, "hot spots" are considered to be generated on AC. The surrounding organic pollutants in aqueous solution can be adsorbed and degraded, through the reactions catalyzed by AC [12,13]. For example, Bo et al. reported the decomposition of p-nitrophenol in solution via MW assisted oxidation process by a granular AC fixed bed [14]. We also reported the degradation kinetics of an azo dye and surfactant in MW/AC system [12,15]. It is known that AC is one of the most commonly used commercial adsorbents in wastewater treatment because of broad-spectrum removal capability towards pollutants, chemical inertness, and thermal stability. However, the application of AC suffers from nonselective adsorption, slow adsorption kinetics, and difficult regeneration. Especially, due to poor selectivity, AC in an amorphous state is not suitable for a continuous-mode wastewater treatment process. Hence, it is necessary to find a replacement adsorbent with higher selective adsorption and better regeneration ability in MW-based remediation process.

Recently, carbon nanotubes (CNTs), as relatively new MW-absorbing material, have been reported as promising materials to remove pollutants in wastewater through adsorption [16–19]. Being different from amorphous AC, CNTs with regular surface can provide one-dimensional and hollow structure, and selective interaction between CNT surface and pollutant molecules [17,18]. Thus, as excellent MW-absorbing materials and adsorbents with a very high selectivity, CNTs can be used as catalyst in MW-based degradation system [19–21]. They can selectively adsorb organic pollutants in aqueous solution when they are treated properly [22–25].

In the present work, an improved method adopting CNTs instead of AC in a MW system is proposed [12,15], in order to improve the degradation kinetics and take full advantage of the activity of catalysts [26]. CNTs can efficiently absorb MW, leading to more "hot spots" formed on CNTs [27]. The organics around "hot spots" can be adsorbed and degraded on CNTs. This work focuses on the effects of MW-induced CNTs-based catalytic degradation of organic pollutants including methyl orange (MO), methylene blue (MB), methyl parathion (MP), sodium dodecyl benzene sulfonate (SDBS), and bisphenol A (BPA) in solution (See Fig. S1). The catalytic activities of CNTs of different diameter under MW irradiation are compared. This is expected to be a rapid and effective technology for the complete elimination of organic pollutants in treating wastewater.

2. Material and methods

2.1. Materials

Multi-walled carbon nanotubes (CNTs) (97% purity) were purchased from Shenzhen Nanoport Co. Ltd., China. Three types of CNTs with length of 5 μm were employed in the study: CNTs (a) diameter of 10–20 nm, surface area of 100–160 m^2/g; CNTs (b) diameter of 20–40 nm, surface area of 80–140 m^2/g; and CNTs (c) diameter of 40–60 nm, surface area of 40–70 m^2/g. Methyl orange (MO), methyl parathion (MP), sodium dodecyl benzene sulfonate (SDBS), bisphenol A (BPA), and methylene blue (MB) were obtained from Sinopharm Chemical Reagent Co. Ltd of Shenyang, China. The reagents were of analytical grade and were used as received. The water employed in all the studies was deionized water (18.2 MΩ·cm) purified by a Milli-Q water system (Millipore Company, USA).

2.2. Pretreatment of CNTs powder

As pretreatment, 2.0 g CNTs powder was weighed and added into 150 mL hydrogen nitrate solution (6.0 mol/L). The mixture was then boiled at 100 °C for 30 min. After cooling to room temperature, the CNTs were filtered and washed repeatedly with deionized water. The washed CNTs powder was filtered out, dried at 105 °C in an oven for 6.0 h, and subjected to grinding. The obtained treated CNTs powder was stored in a desiccator for further use.

2.3. Characterization of pretreated CNTs

The surface morphology and microstructure of the pretreated CNTs with different diameters were characterized using a scanning electron microscope (SEM, JSM-6301F, LEO Corporation, England) at an accelerating voltage of 20 kV. Fourier transform infrared (FTIR) spectra were recorded with a FTIR spectrometer (Nicolet Avatar 330, Nicolet Company, USA) to identify the groups formed on the pretreated CNTs. The scan region was between 4000 and 400 cm^{-1}. Samples were prepared according to the potassium bromide (KBr) slice method with a proportion of 1% to KBr.

2.4. Degradation experiment using MW/CNTs

To examine the catalytic activity of CNTs, degradation experiments were carried out using a controllable MW oven (WD750B, Galanz Company, China) equipped with a self-made glass reactor and a condensing tube. In a typical experiment, a 25 mL MO solution (25 mg/L) at pH 6.0 was mixed with 30.0 mg CNTs powder (1.2 g/L) under constant stirring. The suspension was irradiated by MW (450 W, 2450 MHz). The UV–vis spectra of MO solutions were measured using a UV–vis spectrophotometer (Cary 50, Varian Company, USA). The MO solution was also treated by CNTs only or MW only as controls. Based on the maximum absorbance (at 466 nm) of 0–25 mg/L MO solutions, the % degradation was obtained: % degradation = $[(C_0 - C)/C_0] \times 100\%$. C_0 and C are the initial concentration and concentration after treatment time t of MO solution, respectively. Also, the effects of MW irradiation time (0–7.0 min), initial MO concentration (5.0–45.0 mg/L), CNTs dose (0–2.4 g/L), MW power (0–750 W), initial pH (2.0–10.0) and number of CNTs reuse on the degradation kinetics were examined. The used CNTs powder was separated from the treated solutions and treated adopting water-washing method. In the experiments testing reusability, reused CNTs were evaluated in the treatment of freshly prepared MO solutions. Further, to compare the degradation kinetics of different organic pollutants, several organic contaminants, including MO, methyl parathion (MP), sodium dodecyl benzene sulfonate (SDBS), bisphenol A (BPA), and methylene blue (MB) at 30.44 μmol/L and pH = 6.0 were also treated using 10–20 nm CNTs (0.48 g/L) under MW irradiation (450 W, 2450 MHz) within 7.0 min. The UV–vis spectra of MO solutions were also measured. Based on the maximum absorbance of the MO, MP, SDBS, BPA, and MB solutions at 466 nm, 265 nm, 224 nm, 276 nm, and 662 nm, respectively, the % degradation was also obtained as