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# Desorption and re-adsorption of carbon nanotubes: Comparisons of sodium hydroxide and microwave irradiation processes

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**Abstract**

This study evaluates exhausted carbon nanotubes regenerated by desorption processes using 1 mM NaOH and microwave irradiation processes. Kinetic analyses of re-adsorption were performed using pseudo first- and second-order models. Regression results revealed that a pseudo first-order model accurately captured re-adsorption kinetics. The regeneration efficiency was 28, 30, 35 and 44% at 18, 28, 38 and 48 °C using desorption agent of 1 mM NaOH for 24 h, respectively. Microwave power was considered the most important factor in regeneration experiments, as the temperature reached by exhausted CNTs was directly related to microwave power in this study. Additionally, microwave regeneration was more effective than the desorption agent of NaOH. The most effective conditions for regenerating exhausted CNTs were a microwave power input of 1000 W for 20 min.


*Keywords:* Carbon nanotubes; Re-adsorption; Desorption; Regeneration; Microwaves

## 1. Introduction

Dyes are utilized extensively in textile, leather, paper, and plastic industries. Reactive dyes, which are characterized by their high solubility, cause economic and environmental problems. Removing reactive dyes by coagulation is difficult because most dyes are very soluble in water. Thus, dye removal from colored reactive dye wastewater is crucial to minimizing environmental pollution. Adsorption has been demonstrated to outperform other techniques in treating wastewater—it is low cost, highly efficient, simple, easy to perform and insensitive to toxic substances. Moreover, liquid-phase adsorption is highly efficient in removing dyes from waste effluent.

Carbon nanotubes (CNTs), as a new adsorbent, have attracted considerable attention. Carbon nanotubes are an appealing alternative for removing organic [1–3] and inorganic contaminants from water [4–11] as they have a large specific surface area, small size, with hollow and layered structures. In recent years, new techniques for activated carbon regeneration have attracted considerable interest. Regeneration procedures include thermal treatment [12], chemical extraction [12–14], bio-regeneration [15], supercritical regeneration [16], microwave irradiation [17,18] and ultrasonic regeneration [19–22]. Thermal regeneration is most often applied for regenerating exhausted activated carbon. However, only chemical extraction using NaOH, HCl and $HNO_3$ has been applied to regenerate exhausted CNTs [6,11]. No study has compared various regeneration procedures and investigated the re-adsorption capacity of exhausted CNTs.

During conventional thermal processing, energy is transferred to a material through convection, conduction and radiation of heat from the material surface. Conversely, microwave energy is delivered directly to materials in molecular interactions with the electromagnetic field. This difference in which energy is delivered is responsible for the numerous advantages associated with using microwaves to regenerate exhausted CNTs. This study elucidates and compares regeneration efficiencies of exhausted CNTs under NaOH desorption and microwave irradiation. The effects of temperature on NaOH desorption behaviors were elucidated. Re-adsorption capacities and rates obtained in experimental data were compared with those acquired using pseudo first- and second-order models. The C.I. Reactive Red 2 was employed as the parent compound in all experiments. Study

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objectives are as follows: (i) determine the effects of temperature on NaOH desorption; (ii) evaluate re-adsorption rates using various kinetic models; and, (iii) evaluate regeneration efficiency of the exhausted CNTs using NaOH desorption and microwave irradiation.

## 2. Materials and methods

### 2.1. Materials

The CNTs utilized herein were multi-wall nanotubes generated by pyrolysis of methane gas on Ni particles in chemical vapor deposition (CBT, MWNTs-2040) without further purification. The CNTs were 5–15 μm long, and the mass proportion of amorphous carbon in CNTs was less than 2%. Maximum wavelength ($\lambda_{max}$) of light absorbed by C.I. Reactive Red 2 (Aldrich) was 538 nm.

### 2.2. Adsorption and regeneration experiments

A glass pyramid bottle containing 0.05 g CNTs and 200 ml C.I. Reactive Red 2 solution was placed in a temperature-controlled bath using water shaken at 160 rpm. All experiments used NaOH or $HClO_4$ to adjust the pH of solution. All adsorption experiments were conducted under the condition of 20 mg/l C.I. Reactive Red, 0.25 g/l CNTs, and 24 h of adsorption time at pH 6.5. In the regeneration processes, exhausted CNTs were oven-dried at 105 °C to a constant mass. The concentration of sodium hydroxide (NaOH) used in desorption experiments for regeneration of CNTs was 1 mM. The temperature was maintained at 18, 28, 38 and 48 °C to investigate the effect of temperature on NaOH desorption. An induction microwave oven (max. 3000 W, 2.45 GHz) was the source of microwave radiation. Exhausted CNTs were regenerated under 400, 600, 800, 1000, 1200 and 1400 W microwave irradiation for 10 min to determine the appropriate microwave power. Re-adsorption experiments were performed following the procedure described above. Adsorption of C.I. Reactive Red 2 was determined using a spectrophotometer (Hitachi-U2001) at 538 nm. At equilibrium, suspensions were centrifuged, and the supernatant was filtered through 0.2 μm paper filter for analysis of dye concentrations. Adsorbed amounts, $q_i$, were calculated using the equation, $q_i = (C_0 - C_i)/m$, where $m$ is the amount of CNTs (g/l), and $C_i$ and $C_0$ are initial and equilibrium concentrations (mg/l), respectively.

## 3. Results and discussion

### 3.1. Regeneration of exhausted CNTs by NaOH desorption

#### 3.1.1. Desorption by NaOH at various temperatures

Disposal of exhausted adsorbent is an environmental problem. This study attempted to regenerate exhausted CNTs for reuse using NaOH to desorb the adsorbed dye molecules from CNTs. Fig. 1 presents kinetic analyses of NaOH desorption at different temperatures. The NaOH desorption results were simulated using a first-order kinetic model; Table 1 presents the corresponding constants. Desorption was very rapid during the first hour at every tested temperature, and then slowed abruptly. Desorption rate (0.44–2.30 1/h) and amount (4.1–8.2 mg/g) both increased as temperature increased (18–48 °C) due to NaOH regeneration. Increasing desorption temperature markedly enhanced desorption of C.I. Reactive Red 2 from CNTs; this experimental result is similar to that obtained by Hamdaoui et al. [20,21], who employed ultrasonic desorption to regenerate exhausted granular activated carbon. Li et al. [6] utilized HCl and $HNO_3$ to desorb $Pb^{2+}$ from CNTs. Their experimental results indicated that desorption percentage could reach 100% at pH 2. The highest desorption percentage in this study was about 31%; hence, using acid to desorb heavy metals was easier than desorbing organic compounds. In addition, this result is similar to that obtained by Wang, et al. [10], who studied sorption of $^{243}$Am(III) to multiwall carbon nanotubes and by Chen et al. [11], who using oxidized multiwall carbon nanotubes adsorbed Ni(II) from aqueous solution.

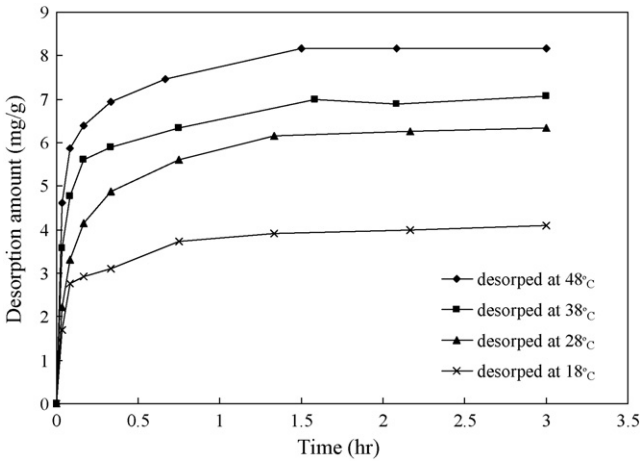


Fig. 1. Kinetic analysis of NaOH regeneration at various temperatures (adsorption: C.I. Reactive Red 2 = 20 mg/l, CNTs = 0.25 g/l, contact time = 24 h and pH = 6.5; desorption: 1 mM NaOH).

#### 3.1.2. Re-adsorption of NaOH-regenerated CNTs

The kinetics of re-adsorption was analyzed at pH 6.5 (Fig. 2). The 3-h re-adsorption capacity of NaOH-regenerated CNTs at 18, 28, 38 and 48 °C was 5.4, 6.3, 7.0 and 8.5 mg/g, respectively. The 3-h amount desorbed by NaOH regeneration at 18, 28, 38 and 48 °C was 4.1, 6.3, 7.1 and 8.2 mg/g, respectively. Desorption amounts and capacity for re-adsorption

Table 1
First-order desorption rate constants of different temperature NaOH desorption (adsorption: dye concentration = 20 mg/l, CNTs = 0.25 g/l and pH = 6.5 for 24 h; desorption: NaOH 1 mM)

| Desorption temperature (°C) | Desorption rate (1/h) | 3 h desorption amount (mg/g) |
|---|---|---|
| 18 | 0.44 (0.993) | 4.1 |
| 28 | 0.69 (0.704) | 6.3 |
| 38 | 1.43 (0.819) | 7.1 |
| 48 | 2.30 (0.993) | 8.2 |

The values in parenthesis are $R^2$.