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.
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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 (λ_{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
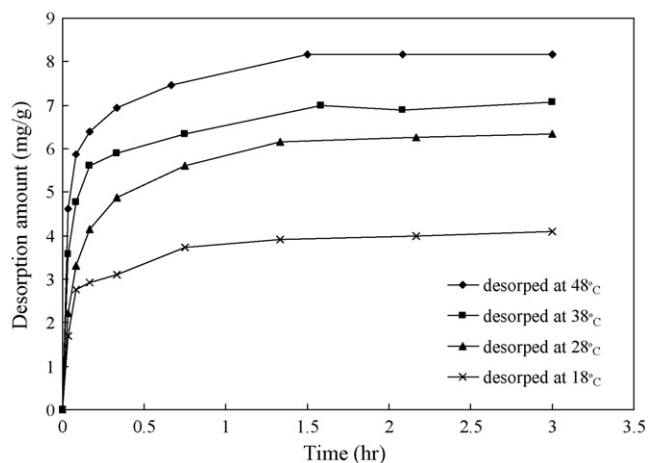

Fig. 1. Kinetic analysis of NaOH regeneration at various temperatures (adsorption: C.I. Reactive Red 2 = 20 mg/l, CNTs = 0.25 g/l, contact time = 24 h and pH = 6.5; desorption: 1 mM NaOH).

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.

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)

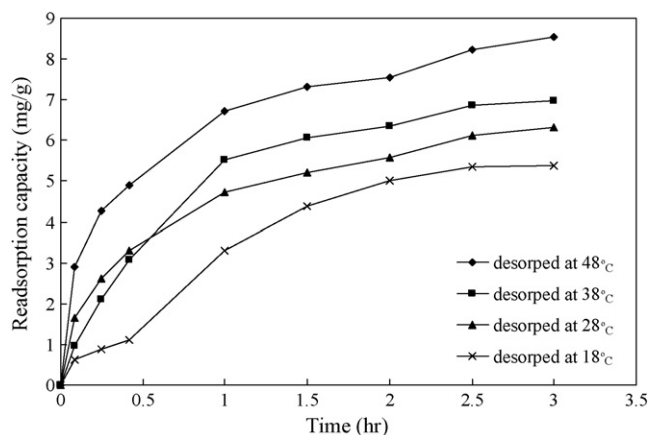| Desorption temperature (°C)	Desorption rate (1/h)	3 h desorption amount (mg/g)
18	0.44 (0.993)	4.1
28	0.69 (0.704)	6.3
38	1.43 (0.819)	7.1
48	2.30 (0.993)	8.2

The values in parenthesis are R^2.

Fig. 2. Kinetic analysis of re-adsorption using NaOH regenerated CNTs (desorption: 1 mM NaOH, contact time = 24 h; re-adsorption: C.I. Reactive Red 2 = 20 mg/l, regenerated CNTs = 0.25 g/l, pH = 6.5 and $T = 28\,^\circ$C).

using NaOH-regenerated CNTs increased as temperature of desorption processes increased. Additionally, the amounts of desorption and re-adsorption were roughly the same, indicating that desorption sites on CNTs can readsorb dye molecules again, similar to fresh sites on CNTs. Re-adsorption is initially rapid, and then slows (Fig. 2)—the remaining vacant surface sites cannot easily be occupied because of the repulsive forces between dye molecules on CNTs [23]. This adsorption phenomenon was the same as that observed by Wu [24], who applied fresh CNTs to adsorb C.I. Reactive Red 2.

Pseudo first- and second-order models were adopted to test experimental data and, thus, elucidate the kinetic re-adsorption process. The pseudo first- and second order models are given by

$$\frac{dq}{dt} = k_1(q_e - q) \tag{1}$$

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{2}$$

where q_e and q are the amounts of C.I. Reactive Red 2 adsorbed on CNTs at equilibrium and at various times t (mg/g), k_1 is the rate constant of the pseudo first-order model for adsorption (1/h),
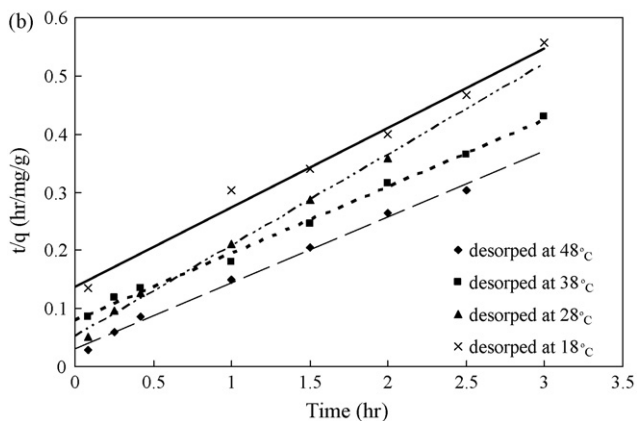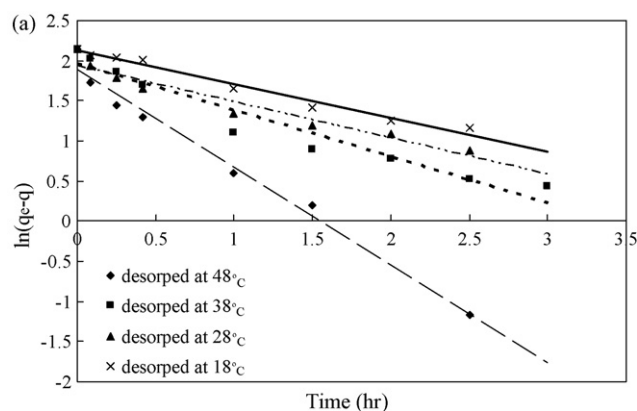

Fig. 3. Regressions of re-adsorption kinetics using NaOH regeneration of CNTs: (a) pseudo first-order model and (b) pseudo second-order model.

and k_2 is the rate constant of the pseudo second-order model for adsorption (g/mg h).

Fig. 3(a) and (b) display the linear regressions to which data (Fig. 2) were fitted using the above models. Table 2 presents the coefficients in the pseudo first- and second-order adsorption kinetic models. Relative errors of q values ($q_{e,cal}$) determined using the pseudo first-order model were more consistent with experimental q values ($q_{e,exp}$) than those calculated using the pseudo second-order model. Furthermore, the R^2 values of

Table 2
Re-adsorption kinetic constants of NaOH regenerated CNTs

Status	$q_{e,exp}$ (mg/g)	k_1 (1/h)	$q_{e,cal}$ (mg/g) (first-order)	k_2 (g/mg h)	$q_{e,cal}$ (mg/g) (second-order)
Original*	26.5	1.78	23.6	0.19	27.9
		(0.976)		(0.990)	
18 °C**	5.4	0.42	8.4	0.14	7.3
		(0.982)		(0.763)	
28 °C**	6.3	0.45	7.0	0.47	6.4
		(0.935)		(0.995)	
38 °C**	7.0	0.58	7.1	0.16	8.7
		(0.941)		(0.996)	
48 °C**	8.5	1.22	6.6	0.42	8.8
		(0.984)		(0.994)	

*Wu [24]; **desorped temperature; the values in parenthesis are R^2; desorption procedure: NaOH 1 mM for 24 h; re-adsorption procedure: dye concentration = 20 mg/l, regenerated CNTs = 0.25 g/l, $T = 28\,^\circ$C and pH = 6.5. The values in parenthesis are R^2.
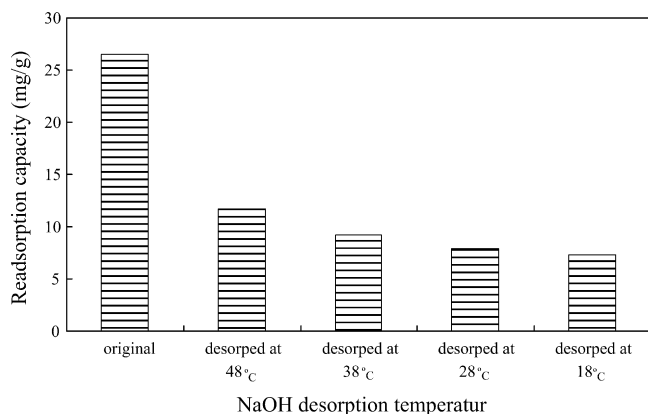
Fig. 4. Saturation re-adsorption capacity of NaOH-regenerated CNTs (desorption: 1 mM NaOH, contact time = 24 h; re-adsorption: C.I. Reactive Red 2 = 20 mg/l, regenerated CNTs = 0.25 g/l, pH = 6.5, contact time = 24 h and $T = 28\,°C$).

the pseudo first-order model exceeded 0.93, implying that the pseudo first-order model more accurately captures re-adsorption kinetics than pseudo second-order model. The re-adsorption capacities and rates of regeneration for CNTs were inferior to those for fresh CNTs. Furthermore, re-adsorption capacities and rates of regeneration for CNTs increased as temperature of desorption using NaOH increased (Table 2). Although the amounts of desorbed and resorbed of C.I. Reactive Red 2 were approximately equal, the amount readsorbed and rate of regeneration for CNTs were worse than those for fresh CNTs. Fig. 4 plots the saturation re-adsorption capacity of NaOH-regenerated CNTs. The 24-h re-adsorption capacities of NaOH-regenerated CNTs at 18, 28, 38 and 48 °C were 7.3, 7.9, 9.3 and 11.7 mg/g, respectively. The differences between re-adsorption capacities at 3 and 24 h at all temperatures were insignificant.

3.2. Regeneration of exhausted CNTs by microwave irradiation

Quan et al. [18] demonstrated the effectiveness of microwave irradiation for regeneration of azo dye-exhausted granular activated carbon (GACs). Liu et al. [17] proposed that when irradiated with 850 W microwaves for 10 min, most pentachlorophenol adsorbed by GACs decomposed to CO_2, H_2O and HCl, Liu et al. also determined that adsorbed GACs could be reused after numerous adsorption/microwave regeneration cycles, and that their adsorption capacity could be maintained a relatively high level. Therefore, microwave irradiation was adopted to regenerate exhausted CNTs in this study.

Microwave power is considered the most important factor in regeneration experiments, as the temperature reached by exhausted CNTs is directly related to microwave power. Microwave power was set at 400, 600, 800, 1000, 1200 and 1400 W and the respective temperatures were 135, 150, 200, 235, 240 and 287 °C after 10 min of microwave irradiation. Increased microwave power input corresponded to increased temperature of exhausted CNTs. When microwave power was 1000 W, the temperature increase was not remarkable. Fig. 5 presents the saturated re-adsorption capacity of regenerated CNTs irradiated at
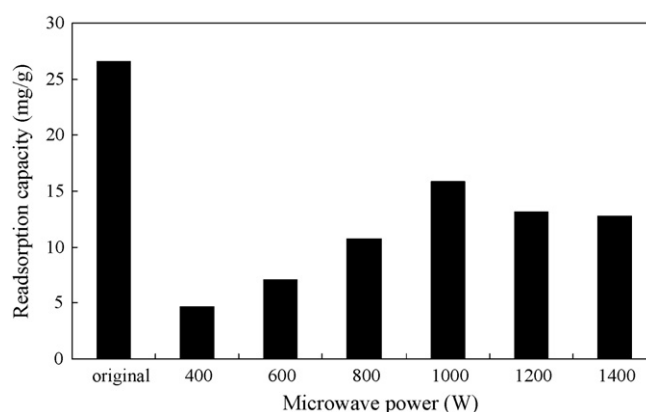

Fig. 5. Regeneration of CNTs irradiated using various microwave powers (C.I. Reactive Red 2 = 20 mg/l, CNTs = 0.25 g/l, contact time = 24 h, $T = 28\,°C$ and microwave irradiation time = 10 min).

various microwave powers. Adsorption capacity of regenerated CNTs was 4.7, 7.1, 10.7, 15.8, 13.1 and 12.8 mg/g after 10 min of irradiation at 400, 600, 800, 1000, 1200 and 1400 W, respectively (Fig. 5). Experimental results demonstrate that 1000 W was the most effective microwave power. Therefore, subsequent experiments were performed to determine the suitable irradiation time with microwave power set at 1000 W. Fig. 6 plots re-adsorption capacity of regenerated CNTs at various microwave irradiation times. Experimental results suggest that re-adsorption capacities were 0.6, 11.7, 15.8, 17.1 and 16.6 mg/g at 0, 5, 10, 20 and 30 min of microwave irradiation (1000 W), respectively. Experimental results also demonstrate that the most appropriate conditions for regenerating exhausted CNTs were a microwave power of 1000 W for 20 min, which generated a re-adsorption efficiency of approximately 64%. The surface chemistry of exhausted CNTs is assumed to change during microwave irradiation, and the change in surface chemistry is assumed to favor re-adsorption of C.I. Reactive Red 2.

Table 3 presents the regeneration efficiency and compares the differences between using NaOH and using microwave irradiation. The highest regeneration efficiency of CNTs (44%)
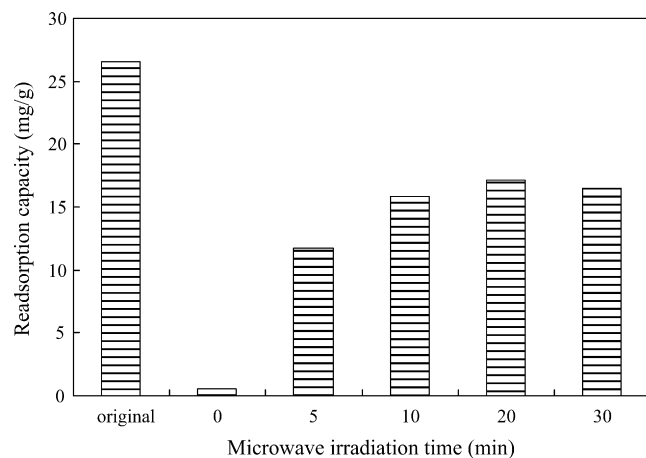

Fig. 6. Effect of microwave irradiation time on regeneration of CNTs (C.I. Reactive Red 2 = 20 mg/l, CNTs = 0.25 g/l, contact time = 24 h, $T = 28\,°C$ and microwave power = 1000 W).

Table 3
Comparison of the regeneration efficiency

Regeneration method		Adsorption capacity after regeneration (mg/g)	Re-adsorption efficiency (%)
NaOH desorption	18 °C	7.3	28
	28 °C	7.9	30
	38 °C	9.3	35
	48 °C	11.7	44
Microwave (10 min)	400 W	4.7	18
	600 W	7.1	27
	800 W	10.7	40
	1000 W	15.8	60
	1200 W	13.1	49
	1400 W	12.8	48
Microwave (1000 W)	5 min	11.7	44
	10 min	15.8	60
	20 min	17.1	64
	30 min	16.5	62

Re-adsorption procedure: dye concentration = 20 mg/l, regenerated CNTs = 0.25 g/l, $T = 28$ °C and pH = 6.5.

for desorption using NaOH was at 48 °C for 24 h; however, 1000 W microwave irradiation for 5 min. yielded a regeneration efficiency of 44%. These experimental results show that microwave irradiation significantly decreased the time needed for regeneration, and regeneration efficiency of microwave irradiation markedly exceeded that for desorption using NaOH. Chiang et al. [12] indicated that regeneration efficiency of chemically treated activated carbon (AC) depends strictly on the characteristics of the adsorbate and the chemical regenerant used. Conversely, regeneration efficiency of thermal treatment did not depend on adsorbate characteristics. Thus, regeneration efficiency associated with thermal treatment exceeded that of associated with chemical treatment.

Ania et al. [25] and Quan et al. [18] found that microwave irradiation reduced the surface area of regenerated AC. However, Liu et al. [17] obtained a contradictory result. Khare et al. [26] observed that proton irradiation of CNTs contains C–H bonds. Liu et al. [17] and Quan et al. [18] determined that microwave irradiation increased the number of mesopores (2–50 nm), thereby increasing the re-adsorption capacity of regenerated AC. Ania et al. [25] observed that microwave irradiation decreased oxygen content and number of mesopores (2–50 nm); these changes were followed by an increase in pH_{zpc}. All these findings establish that microwave irradiation is effective in regenerating exhausted AC. This study did not identify degradation intermediates of adsorbed C.I. Reactive Red 2 or changes in exhausted CNTs caused by microwave irradiation; however, this study demonstrates that microwave irradiation is effective in regenerating exhausted CNTs, which are thus recyclable.

4. Conclusion

This study demonstrated that adsorption of C.I. Reactive Red 2 on CNTs declined as the pH increased. Additionally, the amounts of C.I. Reactive Red 2 desorbed and readsorbed both increased as temperature of desorption processes using NaOH increased. These amounts of desorbed and readsorbed C.I. Reac-

tive Red 2 were almost equal. The adsorption capacity of the regenerated CNTs was 4.7, 7.1, 10.7, 15.8, 13.1 and 12.8 mg/g after 10 min of irradiation at 400, 600, 800, 1000, 1200 and 1400 W, respectively. This study assumed that microwave irradiation slightly alters the surface chemistry of exhausted CNTs, and that change favors re-adsorption of C.I. Reactive Red 2. This study reveals that microwave irradiation markedly decreases the time required for regenerating CNTs; moreover, regeneration efficiency with microwave irradiation substantially exceeded that of desorption using NaOH.

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