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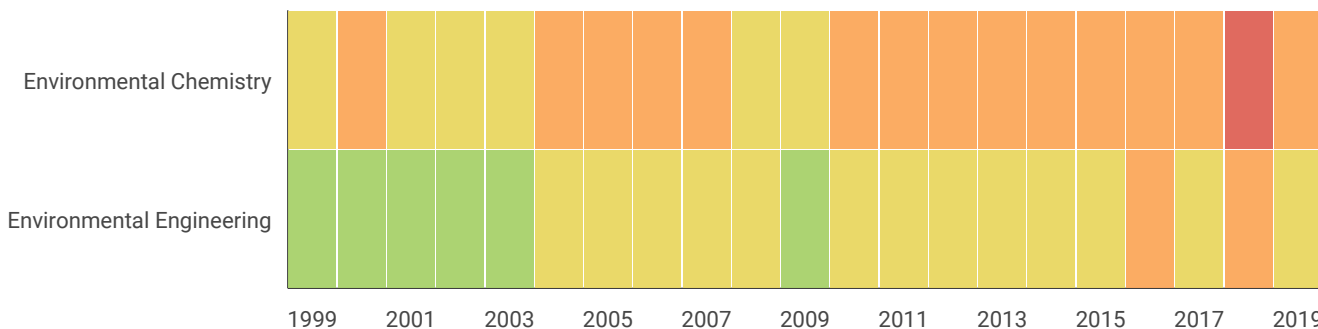|		
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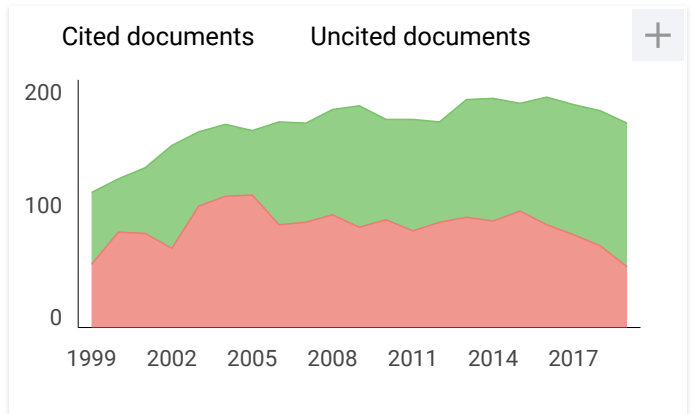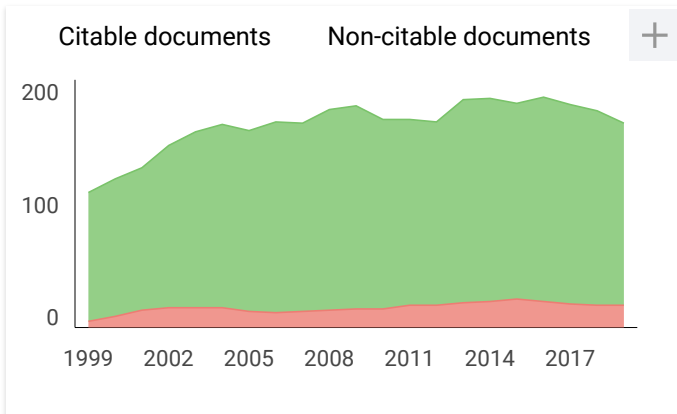💬 Join the conversation about this journal

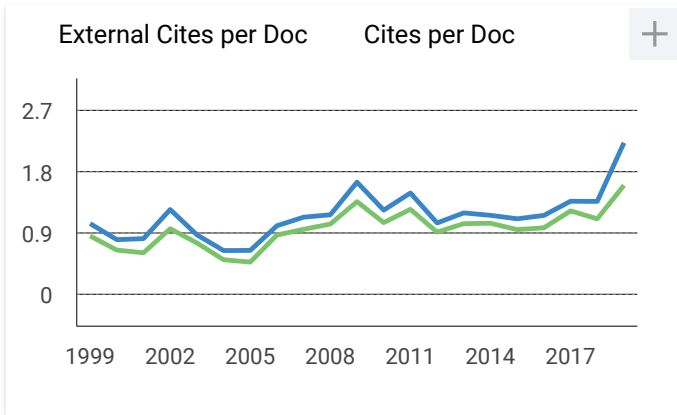Quartiles   ＋

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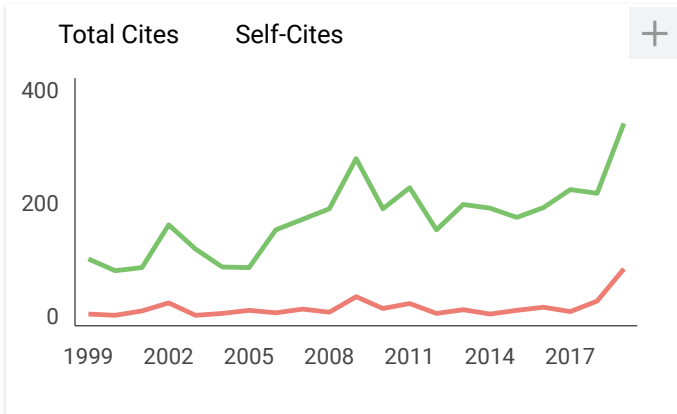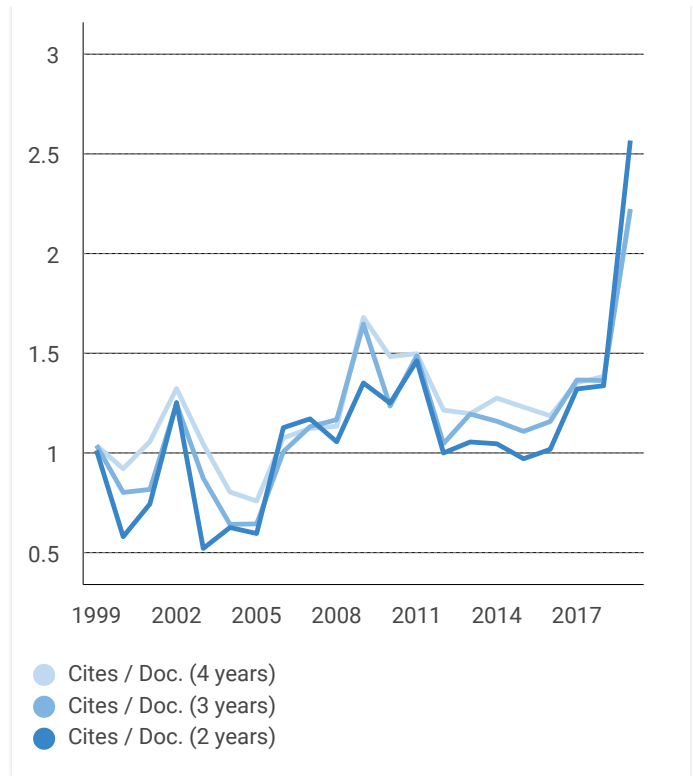## Citable documents   Non-citable documents   +

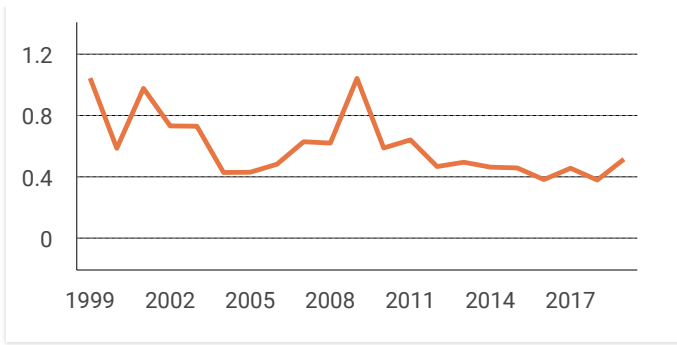## Cited documents   Uncited documents   +
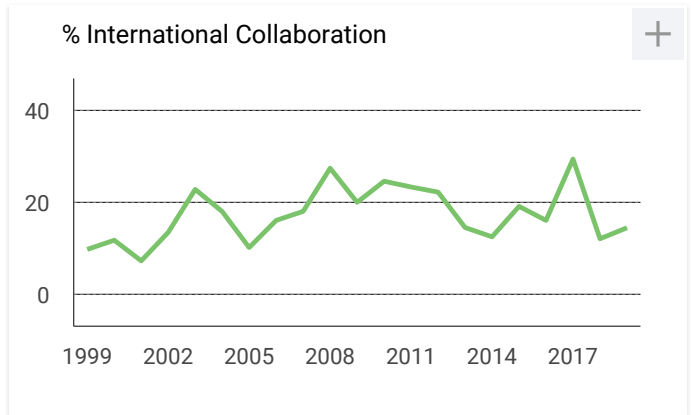
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Multiwalled Carbon Nanotubes for Heterogeneous Nanocatalytic Ozonation

Chedly Tizaoui[a], Haydar Mohammad-Salim[a] & Jono Suhartono[a]

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Multiwalled Carbon Nanotubes for Heterogeneous Nanocatalytic Ozonation

Chedly Tizaoui , Haydar Mohammad-Salim, and Jono Suhartono

Centre for Water Advanced Technologies and Environmental Research (CWATER), College of Engineering, Swansea University, Swansea SA2 8PP, United Kingdom

Multiwalled carbon nanotubes functionalized by plasma oxygen (CNTs) have been used as heterogeneous catalysts for the ozonation of methyl orange (MO) dye (CI 13025) in aqueous solutions. It was found that the addition of CNTs significantly enhanced the dye decolorization as compared to ozone alone or when activated carbon was used at the same dose as CNTs. Both the initial ozone concentration and catalyst dosage enhanced the removal of MO. However, ozone gas concentrations higher than 6 g/m³ NTP did not further improve the decolorization rates. The removal efficiency of MO increased with pH in the range 2 to 3, while a reverse trend was observed when the pH increased from 3 to 9. The addition of a radical scavenger resulted in only a limited change in the decolorization rates suggesting that molecular ozone was the main pathway by which MO decolorization occurred in solution. However, under favorable conditions for MO attraction to CNT surface (pH = 3), the decolorization rate has significantly increased. At higher pH than the pKa value of MO (3.47) and the point of zero charge of CNT (3.87), a condition that favors the electrostatic repulsion of MO from CNT, the rates were reduced in the presence of CNT as compared to ozone alone possibly due to loss of part of the supplied ozone in un-useful parallel reactions.

INTRODUCTION

Over the last decades, many modern treatment techniques such as ozone and UV have been used to treat and purify water

and wastewaters (Kovalova et al. 2013; Loeb et al. 2012; Rice and Hoff 1981; Tizaoui and Grima 2011). The combination of ozone with other additives such as heterogeneous catalysts and hydrogen peroxide results in the production of strong oxidants (i.e., radicals) that enhance even further the performance of the ozone-based systems. Treatment systems that produce hydroxyl radicals in sufficient quantity to affect the oxidation of water are termed as advanced oxidation processes (AOPs) (Glaze et al. 1987). AOPs are generally based on redox mechanisms as a result of losing and gaining electrons by organic molecules and radicals respectively (Rice and Netzer 1983). In the last decades, heterogeneous catalytic ozonation (HCO) has gained significant attention from the research community because of its effectiveness and its practical use (Kasprzyk-Hordern et al. 2003; Legube and Leitner 1999; Li et al. 2010; Mansouri et al. 2013).

Depending on the nature of the catalyst and the operating conditions such as pH and the type of the substance to degrade, some research studies have shown that the degradation takes place via hydroxyl radical reactions and classify HCO as AOPs (Jans and Hoigné 1998), while others have shown that degradation by HCO proceeds mainly via direct reactions of adsorbed molecular ozone or via other radical types than •OH (Kaptijn 1997; Kasprzyk-Hordern et al. 2003). In general, oxidation in heterogeneous catalytic ozonation could occur either on the surface of the catalyst or in the bulk liquid or both. A range of heterogeneous catalysts including activated carbon, metals and metal oxides have been used in HCO (Nawrocki and Kasprzyk-Hordern 2010).

However, despite the potential advantages that carbon nanotubes (CNTs) present in catalytic processes (Serp et al. 2003), they are seldom used in HCO. Because of their extraordinary, chemical, electrical, thermal and mechanical properties (Serp et al. 2003), CNTs are expected to be more suitable than activated carbon (AC), commonly used in HCO, for catalytic applications in liquid phase. The excellent activity of CNTs when used as catalysts or catalyst support

has also been shown for example in catalytic wet air oxidation (Garcia et al. 2005). This suggests that CNTs are expected to enhance ozone reactions and that the rate of such reactions is tunable through CNT functionalization. In addition, functionalization of CNTs via oxidation techniques results in the formation of new sites for hydroxyl radical production that correlates well with the surface oxygen level. Species such as hydroxyl, carboxyl, and carbonyl groups are expected to form during the oxidation of CNTs.

Fan et al. (2014) have shown that in HCO, CNTs changed the distribution of atrazine degradation intermediates, decreasing the effluent toxicity and increasing the mineralization of atrazine though they reduced the rate of atrazine degradation. Other studies (Gonçalves et al. 2013; Liu et al. 2011; Sui et al. 2012) have attempted to identify the mechanisms involved in HCO employing CNTs but due to the limited number of such studies and the variability in conditions used by each study, the effect of CNTs on HCO is still unclear and deserves more in-depth investigations.

In this study, heterogeneous nanocatalytic ozonation (HNCO) using CNTs was investigated for the removal of methyl orange (MO), which is a typical nonbiodegradable azo dye that presents harmful properties to humans and the aquatic life (Diagne et al. 2007; Wang et al. 2008). Evaluation of the kinetics of MO decolorization under different process operating conditions and attempt to determine the mechanisms by

which HCO removes MO as well as comparison of CNTs to activated carbon at the same dose were the main objectives of this study.

MATERIALS AND METHODS
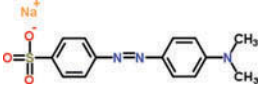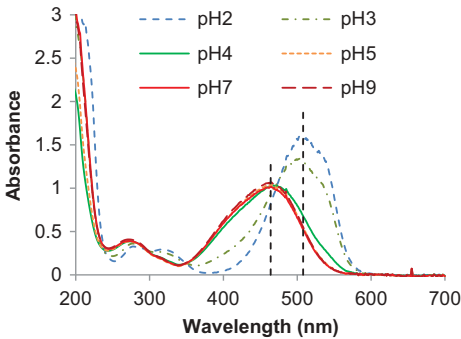
Materials

Methyl orange (MO) was purchased from Fisher Scientific, UK and used as received. The characteristics of MO are shown in Table 1. A stock solution of MO (100 mg/L) was prepared on a daily basis in Milli Q water and other concentrations in the range 10–40 mg/L MO were prepared by dilution of the stock solution. The stock solution was covered by aluminum foil and stored in dark. Multiwalled carbon nanotubes, functionalized by plasma oxygen, was a gift from Haydale Ltd., UK and used as received without further treatment. Properties of the CNTs used are shown in Table 2. Activated carbon was provided by Chemviron, UK and its characteristics were determined in a previous study (Mansouri et al. 2013) and are also summarized in Table 2. Other chemicals of reagent grade were purchased from either Sigma Aldrich, UK or Fisher Scientific, UK.

Experimental Procedures

Ozone was generated from oxygen (compressed gas BOC oxygen cylinder) using an ozone generator (BMT-803,

TABLE 1. Methyl Orange Characteristics

C.I. index	C.I. Acid Orange 52
Systematic name	Sodium 4-([4-(dimethylamino)phenyl]diazenyl)benzenesulfonate
Chemical formula	$C_{14}H_{14}N_3NaO_3S$
Molecular mass	327.34 g/mol
Molecular structure	
pKa	3.47
Spectra at different pH[#]	

λ_{max}	464 nm at pH ≥ 4[#]
	508 nm at pH < 4[#]
Extinction coefficient, ε	$23,362 \pm 1\%$ L.mol^{-1}.cm^{-1} at pH ≥ 4[#]
	30,000–35,000 L.mol^{-1}.cm^{-1} at pH < 4[#]
Color	Yellow orange in alkaline medium and red in acid medium
Uses	Textile industry, indicator in acid-base titrations

[#]Determined in this study.

TABLE 2. Properties of the Carbon Nanotubes and Activated Carbon

Property	Value
Carbon Nanotubes	
Carbon Content (%)	96
Outer Diameter (nm)	~13–16
Length (μm)	~1
Aspect ratio (length/diameter)	~69
Bulk Density (g/cm^3)	~0.19
Oxygen Content (%)	3.5–4
BET surface area (m^2/g)	~250
Activated Carbon	
Particle size (mm)	~1.5
BET surface area (m^2/g)	933
Average pore radius (Å)	11.6
Specific pore volume (cm^3/g)	0.54
pH$_{pzc}$	10.68
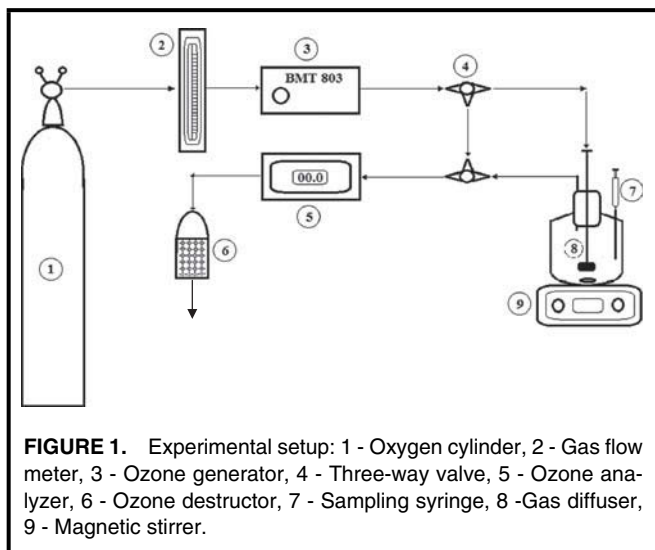
FIGURE 1. Experimental setup: 1 - Oxygen cylinder, 2 - Gas flow meter, 3 - Ozone generator, 4 - Three-way valve, 5 - Ozone analyzer, 6 - Ozone destructor, 7 - Sampling syringe, 8 - Gas diffuser, 9 - Magnetic stirrer.

Tübingen, Germany). The flow rate of oxygen feeding the generator was set at 0.4 L/min and the inlet gas pressure was set at 1.1 bar absolute. The ozone gas concentration was measured by an ozone analyzer (BMT 963 vent). A closed semi-batch reactor was used (Figure 1). The reactor was made from Pyrex glass and fitted with a sample port and a fritted glass gas diffuser. A 150-mL sample of the MO solution at a specific initial concentration was charged into the reactor. The initial pH of the MO solution was adjusted using either 0.1M HNO$_3$ or 0.1M NaOH solutions. Low pH values did not require buffering since the pH did not change significantly during experiment while high pHs required buffering to keep the pH almost constant during experiment.

When used, a given mass of CNTs was also added to the solution immediately before the experiment started. A magnetic stirrer was used for solution mixing. Experiments started after the ozone generator reached stable output as indicated by a constant ozone gas concentration reading from the ozone

analyzer. The exhaust gas was passed through a catalytic destructor containing sodium aluminosilicate to remove any remaining ozone before discharge of the gas to the outside atmosphere via a fume cupboard. A 10-mL glass syringe was used to collect samples at a specific schedule. Immediately after sampling, the samples were exposed to an air stream for about 10 s to stop the reaction by removing any residual ozone in the sample.

Samples containing CNTs were filtered with a syringe filter (0.25-μm pore size) before analysis of the dye concentration. The filter was assessed for possible dye removal in a preliminary study and it was found suitable for the study since no change in dye concentration was observed before and after filtration of a fresh solution. Adsorption experiments were also carried out using different initial MO concentrations (10, 20, 30, and 40 mg/L) while the CNT dose was fixed at 10 mg/L, and the solution volume was set at 150 mL. Freundlich and Langmuir models were used to describe the experimental isotherm data.

Analytical Procedures

Samples collected from the reactor were analyzed using a UV/Vis spectrophotometer (Agilent, HP 8453). MO concentrations were determined from calibration curves obtained at the maximum absorbance wavelength λ_{max} (note: λ_{max} was pH-dependent Table 1). The pH of the solution was determined using a pH meter (FE20-FiveEasy, UK). The molar absorption coefficient of MO at $\lambda_{max} = 464$ nm (pH ≥ 4) was measured to be $23,362 \pm 1\%$ L.mol^{-1}.cm^{-1}, which is comparable to values reported in the literature (Boily and Seward 2005; Chen 2000; Chen et al. 2005).

Characterization of Carbon Nanotubes

In aqueous media, the point of zero charge (pzc) and particle size of CNTs are very important information for adsorption and desorption of contaminants. The particle size of CNTs was measured using a High Performance Particle Sizer 3.3 (Malvern Instrument, UK) at room temperature, pH 5.13 and a 30-min presonication. The zeta potential of CNTs was measured by a Malvern Zetasizer 2000 at room temperature. Five CNT solutions at a concentration of 10 mg/L and pH values of approximately 3, 4, 5, and 7 were used for measuring the CNT point of zero charge (pzc). The pH values of these solutions were adjusted using 0.1M NaOH or 0.1M HNO$_3$.

RESULTS AND DISCUSSION

Characterization of Carbon Nanotubes

The cumulative frequency curve for particle size distribution of CNT is shown in Figure 2a and the change of CNT zeta potential as function of pH is shown in Figure 2b. Figure 2a indicates bimodal distribution with median sizes of 61 nm and 340 nm for the first and second maxima, respectively. The second size dominates in the distribution. The presence of a
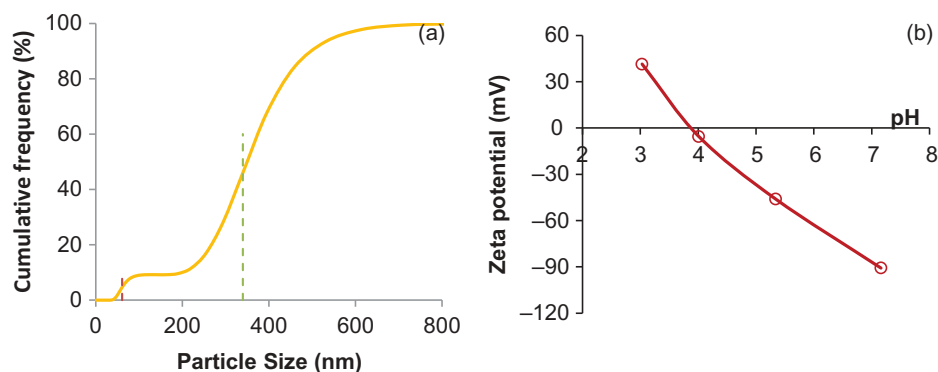
FIGURE 2. CNT characterization (a) cumulative particle size distribution; (b) zeta potential as function of pH.

bimodal distribution indicates that the CNT sample was made up of two populations that may due to incomplete CNT dispersion in the solution. Figure 2b shows that an increase of pH from 3 to 7 results in decrease of the CNT zeta potential. The point of zero charge (pzc) (i.e., zeta potential = 0) was obtained at pH = 3.87, which is comparable to literature (Chen et al. 2008). With further increase of pH above the pzc, the CNT is characterized by a negative zeta potential possibly caused by deprotonated functional groups on the CNT surface such as -COOH and -OH (Rance and Khlobystov 2010).

Removal of Methyl Orange with Adsorption Alone and Ozone Alone

The adsorption of MO on CNTs was found very rapid at the start of the experiment giving an instantaneous drop in MO concentration by about 16% and 30% at CNT concentrations of 20 and 50 mg/L, respectively (Figure 3). The rate of adsorption then levels off and the change of MO concentration by adsorption becomes negligible within the experimental

time frame. Fan et al. (2014), who used atrazine as a model compound, have also found rapid adsorption on CNTs at the beginning of the experiment. The adsorption isotherm of MO on CNTs was well described by a Langmuir type model (data are not shown) with an equation $q^* = 183 \times C/(3.704 + C)$; where q^* is the equilibrium concentration on the CNT in mg/g and C is the liquid equilibrium concentration in mg/L. Based on the Langmuir model, the monolayer maximum MO adsorption capacity of CNT was calculated at 0.56 mmol/g, which is comparable to other studies (Chen et al. 2007; Wang et al. 2013; Yu et al. 2014).

The decolorization of MO solutions with ozone alone was also studied and the results showing the effect of ozone gas concentration are also presented in Figure 3. The figure shows that the decolorization of MO was very rapid at all studied ozone concentrations and as the inlet ozone concentration increased from 2 to 6 g/m³ NTP, the rate of decolorization also increased while a further increase of ozone concentration to 8 g/m³ NTP did not result in appreciable enhancement of the decolorization rate. This indicates that above 6 g/m³ NTP
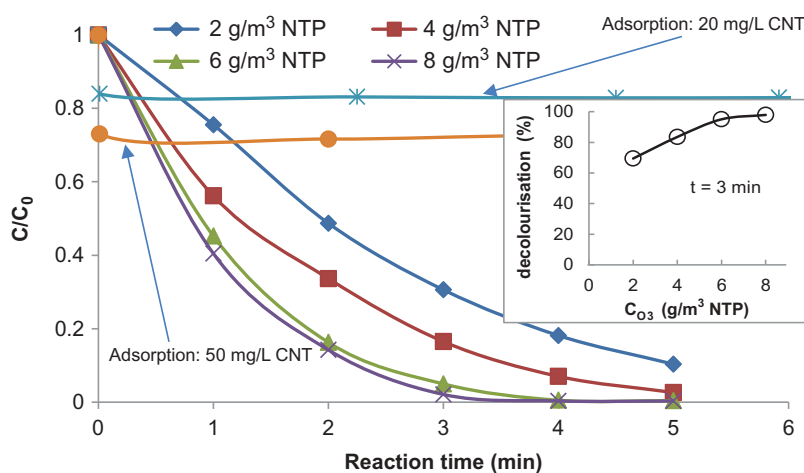
FIGURE 3. Removal of MO by adsorption alone on CNTs and by ozone alone at different concentrations (T = 23 ± 1 °C, pH = 3, C₀ = 20 mg/L).

ozone concentration, the change in removal percentage was minimal indicating a possible optimum ozone concentration was reached. The inset in Figure 3 shows that after 3 min of ozonation, 69% of the initial MO was decolorized at an ozone concentration of only 2 g/m^3 NTP, while ozone concentration of 8 g/m^3 NTP achieved about 98% decolorization after 3 min.

At the four inlet ozone concentrations 2, 4, 6, and 8 g/m^3 NTP, the ratio of the overall ozone supplied to the reactor to the mass of dye removed was calculated and the values were 0.91, 0.63, 0.51, and 0.40 mg MO removed/mg O$_3$ supplied, respectively. Assuming that the observed decrease in MO concentration over time is described by a pseudo-first-order reaction kinetics (Mansouri et al. 2013), the values of the rate constant, k_{obs}, for the different ozone concentrations are shown in Table 3. As the ozone concentration increased to 6 g/m^3 NTP, k_{obs} also increased almost linearly at a rate of 0.162 min^{-1} per g.m^{-3} NTP O$_3$ concentration before it remained almost constant for a concentration higher than 6 g/m^3 NTP. This indicates that operating this system at higher ozone concentrations than 6 g/m^3 NTP will not offer any significant increase in performance, but instead it would result in unnecessary extra energy and oxygen use for the extra ozone production.

TABLE 3. Observed Pseudo–First-Order Reaction Rate Constant

C_{O3} (g/m^3 NTP)	k_{obs} (min^{-1})
0	0.000
2	0.54
4	0.627
6	0.960
8	0.962

T = 23 °C, pH = 3, initial MO concentration C$_0$ = 20 mg/L.

Removal of Methyl Orange with O$_3$/CNTs

The decolorization of MO solution in the absence and presence of CNTs using two different ozone concentrations 2 and 4 g/m^3 NTP is shown in Figure 4. The other experimental conditions were kept the same (initial MO concentration was 20 mg/L, pH 3, room temperature at 23 ± 1 °C and CNTs concentration was 10 mg/L). After 2-min reaction time and at an ozone concentration of only 2 g/m^3 NTP, the decolorization percentage of MO reached 61% in the presence of CNTs while it reached only 51% when ozone alone was used (Figure 4). Increasing ozone concentration to 4 g/m^3 NTP resulted, after 2 min reaction time, in increased decolorization percentages to 77% and 66% in the presence and absence of CNTs, respectively.

This clearly indicates that CNT enhanced the degradation of MO with ozone. Figure 4 inset shows that the addition of CNT has increased the pseudo–first-order rate constant by about a third from that obtained with ozone alone. The enhanced decolorization of MO solutions when CNT was added may due to a combination of adsorption and/or reaction with radical species (e.g., •OH) produced as a result of ozone decomposition in the presence of CNTs. As shown earlier, adsorption contributes to the removal of MO only at the beginning of the experiment with an instantaneous reduction in concentration and the contribution of radicals was assessed using radical scavengers as further discussed here.

Effect of Initial MO Concentration

The effect of initial MO concentration on the decolorization rates using ozone in the absence and presence of CNTs was studied. The kinetics of MO decolorization using ozone alone are shown in Figure 5a, while those obtained in the presence of 10 mg/L CNTs for initial MO concentrations of 10 and 20 mg/L are shown in Figure 5b – for clarity, plots for initial MO concentrations of 30 and
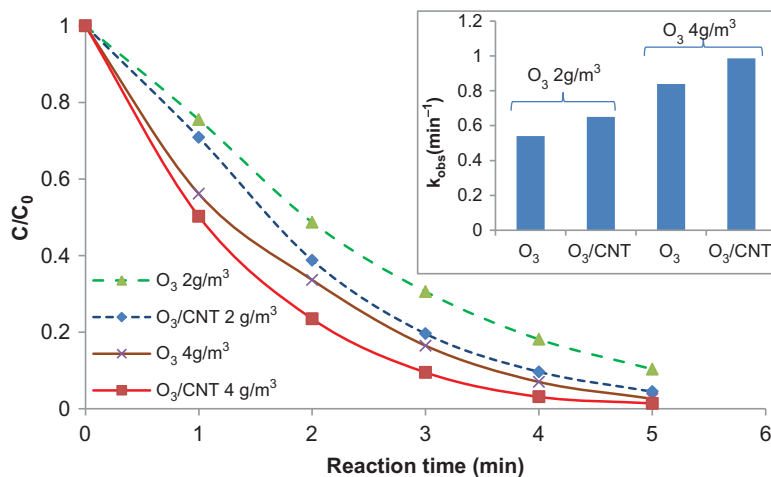

FIGURE 4. Effect of initial ozone concentration on MO decolorization (volume = 150 mL, C$_0$ = 20 mg/L, gas flow rate = 0.4 L/min, CNT = 10 mg/L when used, pH = 3 and temperature = 23 ± 1 °C).
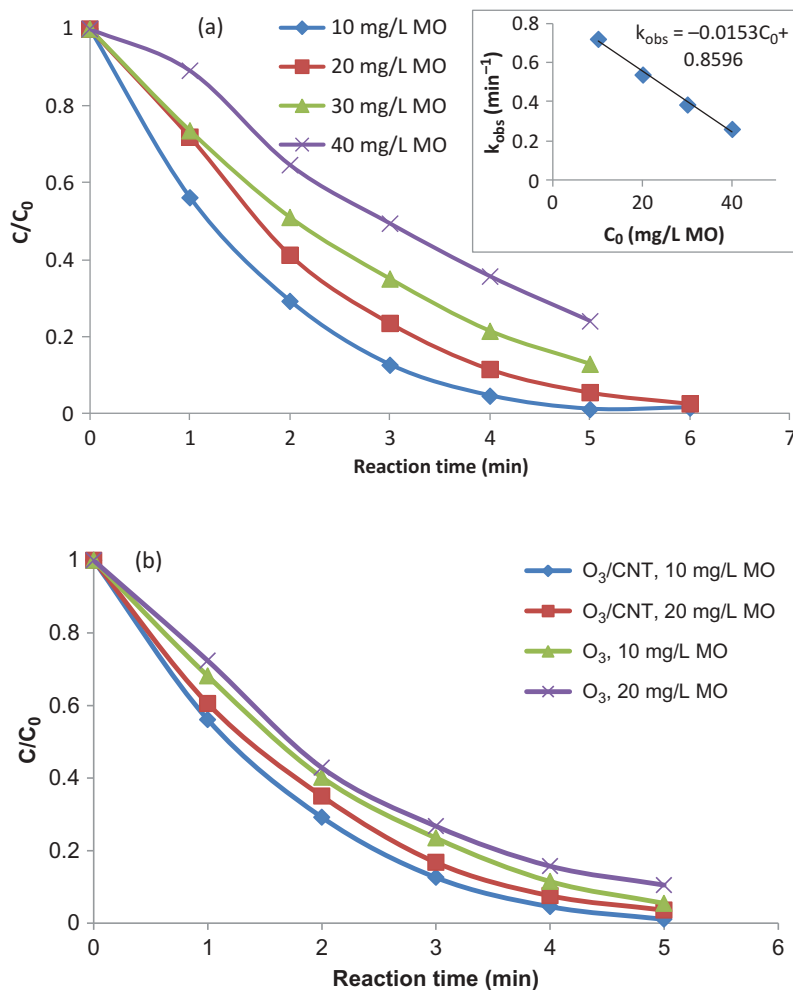
FIGURE 5. Effect of MO concentration on solution decolorization (a) ozone only and (b) comparison between O_3 and O_3/CNT (O_3 gas concentration 2 g/m³ NTP, gas flow rate 0.4 L/min, pH = 3, volume = 150 mL, temperature = 23 ± 1 °C, CNT = 10 mg/L).

40 mg/L are not shown. The results outline that increasing the initial MO concentration reduced the decolorization rates (Figure 5a-b). The decolorization percentage of MO after 3 min reaction time decreased from 77% to 73% and from 87% to 83% following an increase in the initial MO concentrations from 10 to 20 mg/L using ozone in the absence and presence of CNTs respectively. In the absence of CNTs, the observed rate constant, k_{obs}, was found to decrease linearly with increased initial MO concentration at a rate of 0.0153 L.min^{-1}.mg^{-1}. In the presence of 10 mg/L CNT, the reaction kinetics have improved by about 35% and the rate of decrease of the observed rate constant as function of the initial MO concentration was almost equal to that of ozone alone.

Effect of CNT Dose

The dose of catalyst is an important parameter in HCO since it affects the conversion of ozone into radical species as well as it affects the adsorption of the dissolved substances (Mansouri et al. 2013; Sanchez-Polo et al. 2005). The effect of CNT dose on MO decolorization was investigated in this study by varying the CNT dose up to 50 mg/L. Figure 6 shows that as the dose of CNTs increased, the decolorization of MO also increased. For example after 3 min, the removal percentage of MO reached 77% in the absence of CNTs but it increased further to 83% and 90% when the CNT dose increased to 10 and 20 mg/L respectively (Figure 6 inset).

Other studies, which used carbon-based catalysts, have also shown that increasing the catalyst dose resulted in increased degradation rates of HCO processes (Hassan and Hawkyard 2006; Jans and Hoigné 1998; Liu et al. 2011). Assuming that the decolorization rate follows a pseudo–first-order kinetics (Mansouri et al. 2013), the values of the observed rate constant, k_{obs}, are given in Table 4 as function of CNT dose. Table 4 also shows the values of R^2, which are close to one indicating good correlation between the experimental kinetic data and the pseudo–first-order kinetic model. The results in Table 4 show that k_{obs} increased by about 0.011 min^{-1} per 1 mg/L increase in CNT dose.

FIGURE 6. MO removal at different CNT concentrations; inset: removal percentages at reaction time of 3 min (ozone concentration = 2 g/m³ NTP, pH = 3, C_0 = 20 mg/L).

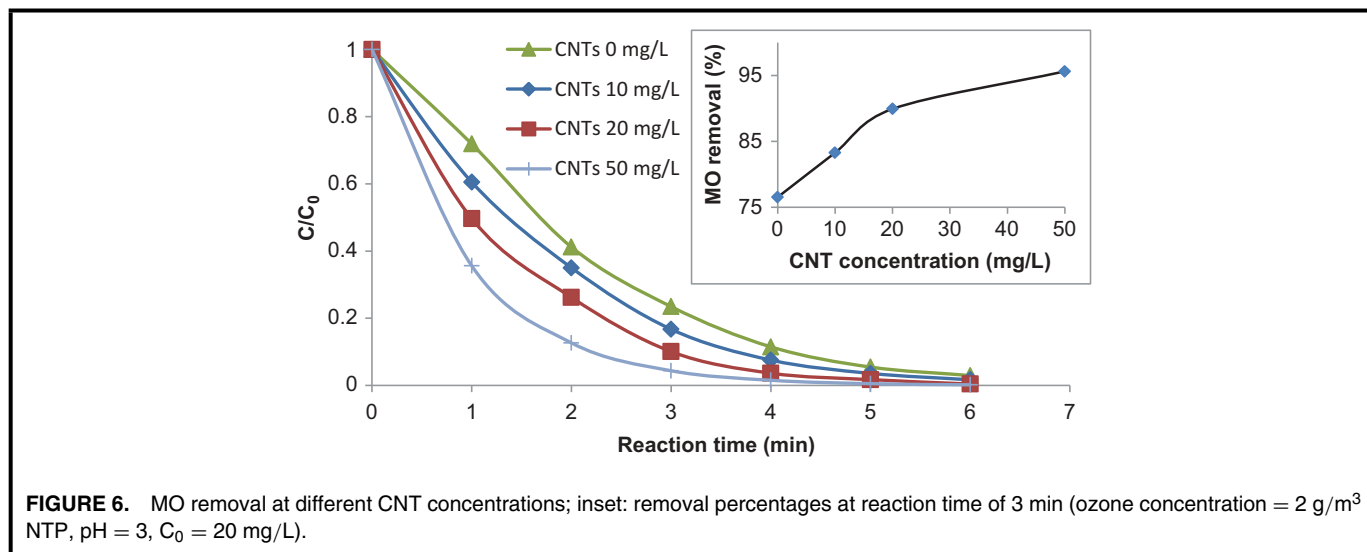**TABLE 4.** Effect of CNT Dose on the Observed First-Order Reaction Rate Constant

CNT dose (mg/L)	k_{obs} (min^{-1})	R^2
0	0.54	0.981
10	0.65	0.990
20	0.79	0.986
50	1.04	0.998

Ozone concentration = 2 g/m³ NTP, pH = 3, C_0 = 20 mg/L.

Effect of pH

The effect of initial pH on the decolorization of MO solutions was studied in the absence and presence of CNTs. At each pH, the decolorization of the MO solution was found to follow a pseudo–first-order kinetics type. The change of the reaction rate constant, k_{obs}, values as function of pH is shown in Figure 7. Initially, when pH increased from 2 to 3, k_{obs} also increased, by about 17% for O₃/CNT and 34% for O₃ alone, but a further increase in pH to 4 resulted in reduction of the rate constant by about 18% for O₃/CNT and by only 2% for O₃ alone. pH 3 appears to give an optimum value of k_{obs}.

Given that the pKa of MO is 3.47 and the pzc of CNTs is 3.87, at pH 2 the non-dissociating form of the MO molecule (AH) dominates (97%) and the surface charge of CNT is positive (Figure 7). MO may interact under these conditions with the surface of CNTs which results in enhancement of the degradation rate as compared to ozone alone (Figure 7, pH 2). A further increase in pH to 3 results in significant increase of the dissociating form of the MO molecule (A⁻) to 25% and the surface of the CNT approaches neutrality but still positive. This environment promotes strong attraction between CNT and MO and results as a consequence in increased rates of MO decolorization. This increase in rate may due to adsorption and reactions with radical species potentially formed via ozone decomposition on CNT surface.

FIGURE 7. Effect of pH on the observed first-order reaction rate constant (ozone concentration = 2 g/m³, C_0 = 20 mg/L, CNT = 10 mg/L).
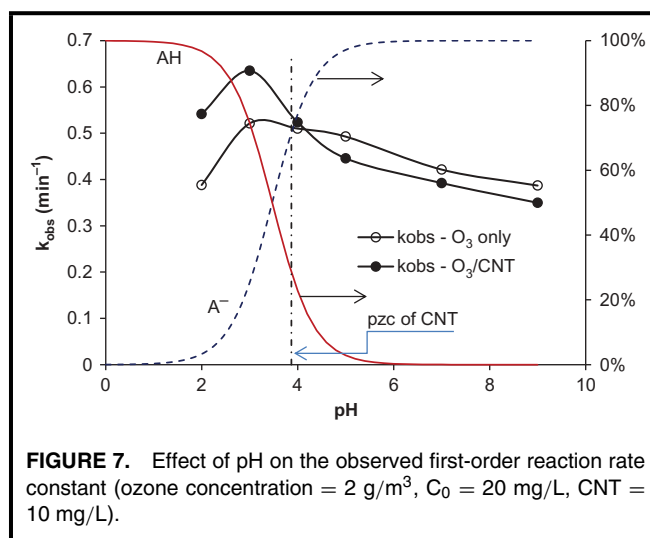
As pH increased to 4 and above, both the CNT surface and the MO molecule become negatively charged, which leads to electrostatic repulsion of the two. Under such conditions, it is unlikely that the MO molecule reaches the surface of the CNT which results in reduction of the rate of MO decolorization at high pH (Figure 7).

Because the dissociating form (A⁻) has a stronger ability for electrophilic substitution reactions than the non-dissociating form (AH), the reactivity of ozone with MO is expected to increase as the pH increases, which explains the observed increase in the rate constant between pH 2 and 3 where A⁻ accounts for 3% at pH 2 but significantly increased to 25% at pH 3 (Figure 7). However, a further increase of pH results in increased ozone decomposition as well and given that ozone reactions with azo-dyes generally proceed in solution via a molecular ozone reaction pathway, the overall observed rate is reduced since the supplied ozone is not totally used in the MO decolorization reaction. Chen

(2000) has also found that the decolorization of MO by ozone was reduced as the pH increased. In addition, part of the supplied ozone may also be involved in parallel reactions on the surface of CNT, which is not accessible to MO molecules at high pH due to repulsion between MO and the CNT surface, leads to reduction in the rate constant of MO decolorization in comparison to ozone alone as observed in Figure 7 when pH > 4.

Effect of Radical Scavenger

Tert-butanol, carbonate/bicarbonate and low pH (i.e., addition of H_3O^+) are the most well-known and commonly used hydroxyl radical (•OH) scavengers, which all have strong effect on the pathway of ozone reactions (Gottschalk et al. 2000; Hoigné et al. 1985). The presence of a radical scavenger in the solution inhibits the radical pathway by quenching the chain reaction which inhibits further formation of hydroxyl radicals and only the molecular ozone reaction pathway (also known as the direct pathway) prevails in the solution. Hydroxyl radicals act as promoters of the chain reaction. The alcohol tert-butanol has been found to alter of the ozone mass transfer (Tizaoui et al. 2009), hence its use as a radical scavenger makes a direct comparison between with and without radical scavenger difficult.

At high pH, the use of carbonate/bicarbonate is hence more plausible; their reaction rate constants with •OH radicals are 3.9×10^8 $M^{-1}.s^{-1}$ and 8.5×10^6 $M^{-1}.s^{-1}$ for carbonate and bicarbonate respectively (Sonntag and von Gunten 2012). Sodium bicarbonate at 0.2 mol/L was used in this study as •OH scavenging agent in the presence of CNTs at 10 mg/L. The observed rate constants of the MO decolorization reaction at pH 3 and pH7 in the presence of bicarbonate are shown in Table 5. It can be calculated from Table 5 that the addition of bicarbonate has reduced k_{obs} by small percentages; 8% and 16% at pH 3 and 7, respectively. Because at pH 3, bicarbonate becomes carbonic acid, which has negligible •OH scavenging effects, the small reduction in k_{obs} at pH 3 may be due only to experimental errors.

The results suggest that overall the contribution of hydroxyl radicals to the decolorization of MO is minimal and the main reaction pathway by which MO decolorizes is molecular ozone. According to Table 4, the addition of 10 mg/L CNT at pH 3, increased k_{obs} by about 22% from that of ozone alone. It can hence be suggested that the increased k_{obs} in the presence of CNT at pH 3 was due mainly to a

TABLE 5. Effect of Hydroxyl Radical Scavenger (Bicarbonate) on the Observed First-Order Reaction Rate Constant

k_{obs} at pH 3 (min^{-1})		k_{obs} at pH 7 (min^{-1})	
Without bicarbonate	0.65	Without bicarbonate	0.39
With bicarbonate	0.60	With bicarbonate	0.33

Ozone gas concentration = 2 g/m^3, pH = 3 and 7, C_0 = 20 mg/L, CNT = 10 mg/L.

TABLE 6. Comparison Between CNT and AC as Catalysts in Heterogeneous Catalytic Ozonation

System	K_{obs} (min^{-1})
O_3 alone	0.54
O_3/AC	0.56
O_3/CNT	0.65

Ozone gas concentration = 2 g/m^3, C_0 = 20 mg/L, pH = 3, CNT dose = 10 mg/L, AC dose = 10 mg/L.

heterogeneous catalytic phenomenon by which CNT attracted both ozone and MO to its surface where the reaction took place (Beltran et al. 2002). Hassan and Hawkyard (2006) have also concluded that catalytic ozone decomposition by activated carbon improved color decolorization of dyes. Given that the hydroxyl radical scavenger had minimal effect, it can therefore be concluded that the decolorization of MO with O_3/CNT is mainly due to molecular ozone reaction and the CNT plays an important role in enhancing the reaction rate only when the operating conditions are favorable for MO attraction to the CNT surface (i.e., pH 3).

Comparison between CNT and Activated Carbon

A comparison between CNT and activated carbon (AC) was made in this study using a dose of 10 mg/L of each catalyst. The decolorization rate in the presence of AC was also modeled by a pseudo–first-order kinetics (Mansouri et al. 2013) and the observed rate constants are presented in Table 6 for each case. At pH 3, the addition of AC improved k_{obs} by approximately 3% whilst the addition of CNT increased k_{obs} by 22% as compared to k_{obs} obtained when ozone alone was used. This indicates that on a mass basis CNT improved the MO decolorization by about 7 times more than AC. Larger doses of AC are then required to achieve MO decolorization comparable to that obtained by CNT. It can therefore be suggested that CNT-based heterogeneous catalytic ozonation offers an efficient alternative for wastewater treatment.

CONCLUSIONS

The removal of methyl orange (MO) using ozone in the presence and absence of multiwalled carbon nanotubes (CNTs) was studied in this research under different operating conditions. The operating conditions were initial concentration of MO, initial concentration of ozone, pH, radical scavenger, catalyst dosage and AC. The most effective improvements on the MO decolorization were observed when CNT was used at pH 3 and at increased ozone concentration and CNT doses. An inlet ozone gas concentration of 6 g/m^3 NTP seems optimal since higher inlet concentrations resulted in insignificant change of the decolorization rates. Molecular ozone reaction was found to dominate the pathway by which MO decolorization occurred in solution and the contribution of •OH was suggested as minimal.

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The CNT was found to play an important role in enhancing the reaction rate only when the operating conditions are favorable for surface attraction of the MO molecule by CNT surface and this when pH = 3. Higher pH values than 3 resulted in reduction of the decolorization rates, possibly due to loss of part of the supplied ozone in parallel reactions of insignificant importance to the decolorization of MO. Comparing activated carbon to CNTs, it was found that at the same dose, CNTs enhanced the decolorization rates by approximately 7 times more than AC relative to ozone alone. The study suggests that O_3/CNTs can be used as an effective treatment system for wastewaters.

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