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### **Paper:**

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# 1       **Multi-walled carbon nanotubes for heterogeneous nanocatalytic ozonation**

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6       1792 295676.

7       **Shortened title:** Heterogeneous nanocatalytic ozonation

## 8       **Abstract**

9       Multi-walled carbon nanotubes functionalised by plasma oxygen (CNTs) have been used as  
10       heterogeneous catalysts for the ozonation of methyl orange (MO) dye (CI 13025) in aqueous  
11       solutions. It was found that the addition of CNTs significantly enhanced the dye  
12       decolourisation as compared to ozone alone or when activated carbon was used at the  
13       same dose as CNTs. Both the initial ozone concentration and catalyst dosage enhanced the  
14       removal of MO. However, ozone gas concentrations higher than 6 g/m<sup>3</sup> NTP did not improve  
15       any further the decolourisation rates. The removal efficiency of MO increased with pH in the  
16       range 2 to 3, while a reverse trend was observed when the pH increased from 3 to 9. The  
17       addition of a radical scavenger resulted in only a limited change in the decolourisation rates  
18       suggesting that molecular ozone was the main pathway by which MO decolourisation  
19       occurred in solution. However, under favourable conditions for MO attraction to CNT surface  
20       (pH=3), the decolourisation rate has significantly increased. At higher pH than the pKa value  
21       of MO (3.47) and the point of zero charge of CNT (3.87), a condition that favours the  
22       electrostatic repulsion of MO from CNT, the rates were reduced in the presence of CNT as  
23       compared to ozone alone possibly due to loss of part of the supplied ozone in un-useful  
24       parallel reactions.  
25       parallel reactions.

26       **Key-words:** Ozone, Advanced oxidation, Multi-walled carbon nanotube, Catalytic ozonation,  
27       Nanocatalysis, Methyl orange dye.

## 1 **Introduction**

2 Over the last decades, many modern treatment techniques such as ozone and UV have  
3 been used to treat and purify water and wastewaters (Rice and Hoff, 1981; Tizaoui and  
4 Grima, 2011; Loeb et al., 2012; Kovalova et al., 2013). The combination of ozone with other  
5 additives such as heterogeneous catalysts and hydrogen peroxide results in the production  
6 of strong oxidants (i.e. radicals) that enhance even further the performance of the ozone-  
7 based systems. Treatment systems that produce hydroxyl radicals in sufficient quantity to  
8 affect the oxidation of water are termed as Advanced Oxidation Processes (AOPs) (Glaze et  
9 al., 1987). AOPs are generally based on redox mechanisms as a result of losing and gaining  
10 electrons by organic molecules and radicals respectively (Rice and Netzer, 1983). In the last  
11 decades, heterogeneous catalytic ozonation (HCO) has gained significant attention from the  
12 research community because of its effectiveness and its practical use (Legube and Leitner,  
13 1999; Kasprzyk-Hordern et al., 2003; Li et al., 2010; Mansouri et al., 2013). Depending on  
14 the nature of the catalyst and the operating conditions such as pH and the type of the  
15 substance to degrade, some research studies have shown that the degradation takes place  
16 via hydroxyl radical reactions and classify HCO as AOPs (Jans and Hoigne, 1998), whilst  
17 others have shown that degradation by HCO proceeds mainly via direct reactions of  
18 adsorbed molecular ozone or via other radical types than  $\cdot\text{OH}$  (Kaptijn, 1997; Kasprzyk-  
19 Hordern et al., 2003). In general, oxidation in heterogeneous catalytic ozonation could occur  
20 either on the surface of the catalyst or in the bulk liquid or both. A range of heterogeneous  
21 catalysts including activated carbon, metals and metal oxides have been used in HCO  
22 (Nawrocki and Kasprzyk-Hordern, 2010). However, despite the potential advantages that  
23 carbon nanotubes (CNTs) present in catalytic processes (Serp et al., 2003), they are seldom  
24 used in HCO. Because of their extraordinary, chemical, electrical, thermal and mechanical  
25 properties (Serp et al., 2003), CNTs are expected to be more suitable than activated carbon  
26 (AC), commonly used in HCO, for catalytic applications in liquid phase. The excellent activity  
27 of CNTs when used as catalysts or catalyst support has also been shown for example in

1 catalytic wet air oxidation (Garcia et al., 2005). This suggests that CNTs are expected to  
2 enhance ozone reactions and that the rate of such reactions is tunable through CNT  
3 functionalisation. In addition, functionalisation of CNTs via oxidation techniques results in the  
4 formation of new sites for hydroxyl radical production that correlates well with the surface  
5 oxygen level. Species such as hydroxyl, carboxyl, and carbonyl groups are expected to form  
6 during the oxidation of CNTs. Fan et al. (2014) have shown that in HCO, CNTs changed the  
7 distribution of atrazine degradation intermediates, decreasing the effluent toxicity and  
8 increasing the mineralisation of atrazine though they reduced the rate of atrazine  
9 degradation. Other studies (Liu et al., 2011; Sui et al., 2012; Gonçalves et al., 2013) have  
10 attempted to identify the mechanisms involved in HCO employing CNTs but due to the  
11 limited number of such studies and the variability in conditions used by each study, the effect  
12 of CNTs on HCO is still unclear and deserves more in depth investigations.

13

14 In this study, heterogeneous nanocatalytic ozonation (HNCO) using CNTs was investigated  
15 for the removal of methyl orange (MO), which is a typical non-biodegradable azo dye that  
16 presents harmful properties to humans and the aquatic life (Diagne et al., 2007; Wang et al.,  
17 2008). Evaluation of the kinetics of MO decolourisation under different process operating  
18 conditions and attempt to determine the mechanisms by which HCO removes MO as well as  
19 comparison of CNTs to activated carbon at the same dose were the main objectives of this  
20 study.

21

## 22 **Materials and methods**

### 23 *Materials*

24

25 Methyl orange (MO) was purchased from Fisher Scientific, UK and used as received. The  
26 characteristics of MO are shown in Table 1. A stock solution of MO (100 mg/L) was prepared  
27 on a daily basis in Milli Q water and other concentrations in the range 10-40 mg/L MO were

1 prepared by dilution of the stock solution. The stock solution was covered by aluminium foil  
2 and stored in dark. Multi-walled carbon nanotubes, functionalised by plasma oxygen, was a  
3 gift from Haydale Ltd., UK and used as received without further treatment. Properties of the  
4 CNTs used are shown in Table 2. Activated carbon was provided by Chemviron, UK and its  
5 characteristics were determined in a previous study (Mansouri et al., 2013) and are also  
6 summarised in Table 2. Other chemicals of reagent grade were purchased from either  
7 Sigma Aldrich, UK or Fisher Scientific, UK.

8 **Table 1**

9  
10 **Table 2**

11  
12  
13 *Experimental Procedures*

14  
15 Ozone was generated from oxygen (compressed gas BOC oxygen cylinder) using an ozone  
16 generator (BMT-803). The flow rate of oxygen feeding the generator was set at 0.4 L/min  
17 and the inlet gas pressure was set at 1.1 bar absolute. The ozone gas concentration was  
18 measured by an ozone analyser (BMT 963 vent). A closed semi-batch reactor was used  
19 (Figure 1). The reactor was made from Pyrex glass and fitted with a sample port and a fritted  
20 glass gas diffuser. A 150 mL of the MO solution at a specific initial concentration was  
21 charged into the reactor. The initial pH of the MO solution was adjusted using either 0.1M  
22 HNO<sub>3</sub> or 0.1M NaOH solutions. Low pH values did not require buffering since the pH did not  
23 change significantly during experiment whilst high pHs required buffering to keep the pH  
24 almost constant during experiment. When used, a given mass of CNTs was also added to  
25 the solution immediately before the experiment started. A magnetic stirrer was used for  
26 solution mixing. Experiments started after the ozone generator reached stable output as  
27 indicated by a constant ozone gas concentration reading from the ozone analyser. The  
28 exhaust gas was passed through a catalytic destructor containing sodium aluminosilicate to

1 remove any remaining ozone before discharge of the gas to the outside atmosphere via a  
2 fumecupboard. A 10 mL glass syringe was used to collect samples at a specific schedule.  
3 Immediately after sampling, the samples were exposed to an air stream for about 10  
4 seconds to stop the reaction by removing any residual ozone in the sample. Samples  
5 containing CNTs were filtered with a syringe filter (0.25  $\mu\text{m}$  pore size) before analysis of the  
6 dye concentration. The filter was assessed for possible dye removal in a preliminary study  
7 and it was found suitable for the study since no change in dye concentration was observed  
8 before and after filtration of a fresh solution. Adsorption experiments were also carried out  
9 using different initial MO concentrations (10, 20, 30 and 40 mg/L) whilst the CNT dose was  
10 fixed at 10 mg/L and the solution volume was set at 150 mL. Freundlich and Langmuir  
11 models were used to describe the experimental isotherm data.

12

13

### Figure 1

14

15

#### *Analytical procedures*

17

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

25

#### *Characterisation of carbon nanotubes*

27

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

9

## 10 **Results and discussion**

11

### 12 ***Characterisation of carbon nanotubes***

13

14 The cumulative frequency curve for particle size distribution of CNT is shown in Figure 2(a)  
15 and the change of CNT zeta potential as function of pH is shown in Figure 2(b). Figure 2(a)  
16 indicates bimodal distribution with median sizes of 61 nm and 340 nm for the first and  
17 second maxima respectively. The second size dominates in the distribution. The presence of  
18 a bimodal distribution indicates that the CNT sample was made up of two populations that  
19 may due to incomplete CNT dispersion in the solution. Figure 2(b) shows that an increase of  
20 pH from 3 to 7 results in decrease of the CNT zeta potential. The point of zero charge (pzc)  
21 (i.e. zeta potential = 0) was obtained at pH = 3.87, which is comparable to literature (Chen et  
22 al., 2008). With further increase of pH above the pzc, the CNT is characterised by a negative  
23 zeta potential possibly caused by deprotonated functional groups on the CNT surface such  
24 as -COOH and -OH (Rance and Khlobystov, 2010).

25

26

27

**Figure 2**

## 1 **Removal of methyl orange with adsorption alone and ozone alone**

2

3 The adsorption of MO on CNTs was found very rapid at the start of the experiment giving an  
4 instantaneous drop in MO concentration by about 16% and 30% at CNT concentrations of  
5 20 and 50 mg/L respectively (Figure 3). The rate of adsorption then levels off and the  
6 change of MO concentration by adsorption becomes negligible within the experimental time  
7 frame. Fan et al. (2014), who used atrazine as a model compound, have also found rapid  
8 adsorption on CNTs at the beginning of the experiment. The adsorption isotherm of MO on  
9 CNTs was well described by a Langmuir type model (data are not shown) with an equation  
10  $q^* = 183 \times C / (3.704 + C)$ ; where  $q^*$  is the equilibrium concentration on the CNT in mg/g and C is  
11 the liquid equilibrium concentration in mg/L. Based on the Langmuir model, the monolayer  
12 maximum MO adsorption capacity of CNT was calculated at 0.56 mmol/g, which is  
13 comparable to other studies (Chen et al., 2007; Wang et al., 2013; Yu et al., 2014).

14

15 The decolourisation of MO solutions with ozone alone was also studied and the results  
16 showing the effect of ozone gas concentration are also presented on Figure 3. The figure  
17 shows that the decolourisation of MO was very rapid at all studied ozone concentrations and  
18 as the inlet ozone concentration increased from 2 to 6 g/m<sup>3</sup> NTP, the rate of decolourisation  
19 also increased while a further increase of ozone concentration to 8 g/m<sup>3</sup> NTP did not result  
20 in appreciable enhancement of the decolourisation rate. This indicates that above 6 g/m<sup>3</sup>  
21 NTP ozone concentration, the change in removal percentage was minimal indicating a  
22 possible optimum ozone concentration was reached. The inset in Figure 3 shows that after 3  
23 minutes of ozonation, 69% of the initial MO was decolourised at an ozone concentration of  
24 only 2 g/m<sup>3</sup> NTP while ozone concentration of 8 g/m<sup>3</sup> NTP achieved about 98%  
25 decolourisation after 3 minutes.

26 At the four inlet ozone concentrations 2, 4, 6 and 8 g/m<sup>3</sup> NTP, the ratio of the overall ozone  
27 supplied to the reactor to the mass of dye removed was calculated and the values were  
28 0.91, 0.63, 0.51 and 0.40 mg MO removed/mg O<sub>3</sub> supplied respectively. Assuming that the

1 observed decrease in MO concentration over time is described by a pseudo-first-order  
2 reaction kinetics (Mansouri et al., 2013), the values of the rate constant,  $k_{obs}$ , for the different  
3 ozone concentrations are shown in Table 3. As the ozone concentration increased to 6 g/m<sup>3</sup>  
4 NTP,  $k_{obs}$  also increased almost linearly at a rate of 0.162 (min<sup>-1</sup>/g.m<sup>-3</sup>) before it remained  
5 almost constant for a concentration higher than 6 g/m<sup>3</sup> NTP. This indicates that operating  
6 this system at higher ozone concentrations than 6 g/m<sup>3</sup> NTP will not offer any significant  
7 increase in performance but instead it would result in unnecessary extra energy and oxygen  
8 use for the extra ozone production.

9

10

**Table 3**

11

12

**Figure 3**

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### 15 ***Removal of methyl orange with O<sub>3</sub>/CNTs***

16

17 The decolourisation of MO solution in the absence and presence of CNTs using two different  
18 ozone concentrations 2 and 4 g/m<sup>3</sup> NTP is shown in Figure 4. The other experimental  
19 conditions were kept the same (initial MO concentration was 20 mg/L, pH 3, room  
20 temperature at 23±1°C and CNTs concentration was 10 mg/L). After 2 minutes reaction time  
21 and at an ozone concentration of only 2 g/m<sup>3</sup> NTP, the decolourisation percentage of MO  
22 reached 61% in the presence of CNTs while it reached only 51% when ozone alone was  
23 used (Figure 4). Increasing ozone concentration to 4 g/m<sup>3</sup> NTP resulted, after 2 minutes  
24 reaction time, in increased decolourisation percentages to 77% and 66% in the presence  
25 and absence of CNTs respectively. This clearly indicates that CNT enhanced the  
26 degradation of MO with ozone. Figure 4 inset shows that the addition of CNT has increased  
27 the pseudo-first-order rate constant by about a third from that obtained with ozone alone.

1 The enhanced decolourisation of MO solutions when CNT was added may due to a  
2 combination of adsorption and/or reaction with radical species (e.g.  $\cdot\text{OH}$ ) produced as a  
3 result of ozone decomposition in the presence of CNTs. As shown earlier, adsorption  
4 contributes to the removal of MO only at the beginning of the experiment with an  
5 instantaneous reduction in concentration and the contribution of radicals was assessed  
6 using radical scavengers as further discussed in the paper.

7

8

9

#### Figure 4

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#### 12 ***Effect of initial MO concentration***

13

14 The effect of initial MO concentration on the decolourisation rates using ozone in the  
15 absence and presence of CNTs was studied. The kinetics of MO decolourisation using  
16 ozone alone are shown in Figure 5(a) while those obtained in the presence of 10 mg/L CNTs  
17 for initial MO concentrations of 10 and 20 mg/L are shown in Figure 5(b) – for clarity, plots  
18 for initial MO concentrations of 30 and 40 mg/L are not shown. The results outline that  
19 increasing the initial MO concentration reduced the decolourisation rates (Figure 5 a-b). The  
20 decolourisation percentage of MO after 3 min reaction time decreased from 77% to 73% and  
21 from 87% to 83% following an increase in the initial MO concentrations from 10 to 20 mg/L  
22 using ozone in the absence and presence of CNTs respectively. In the absence of CNTs, the  
23 observed rate constant,  $k_{obs}$ , was found to decrease linearly with increased initial MO  
24 concentration at a rate of  $0.0153 \text{ L}\cdot\text{min}^{-1}\cdot\text{mg}^{-1}$ . In the presence of 10 mg/L CNT, the reaction  
25 kinetics have improved by about 35% and the rate of decrease of the observed rate constant  
26 as function of the initial MO concentration was almost equal to that of ozone alone.

27

28

## Figure 5

### **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 (Sanchez-Polo et al., 2005; Mansouri et al., 2013). The effect of CNT dose on MO decolourisation 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 decolourisation of MO also increased. For example after 3 minutes, 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, who used a carbon-based catalysts, have also shown that increasing the catalyst dose resulted in increased degradation rates of HCO processes (Jans and Hoigne, 1998; Hassan and Hawkyard, 2006; Liu et al., 2011). Assuming that the decolourisation 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  $0.011 \text{ min}^{-1}$  per 1mg/L increase in CNT dose.

### Table 4

### Figure 6

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## **Effect of pH**

The effect of initial pH on the decolourisation of MO solutions was studied in the absence and presence of CNTs. At each pH, the decolourisation 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 O<sub>3</sub>/CNT and 34% for O<sub>3</sub> alone, but a further increase in pH to 4 resulted in reduction of the rate constant by about 18% for O<sub>3</sub>/CNT and by only 2% for O<sub>3</sub> 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<sup>-</sup>) 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 decolourisation. This increase in rate may due to adsorption and reactions with radical species potentially formed via ozone decomposition on CNT surface. 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 and this results in reduction of the rate of MO decolourisation at high pH (Figure 7). Since the dissociating form (A<sup>-</sup>) 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<sup>-</sup> 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

1 generally proceed in solution via a molecular ozone reaction pathway, the overall observed  
2 rate is reduced since the supplied ozone is not totally used in the MO decolourisation  
3 reaction. Chen (2000) has also found that the decolourisation of MO by ozone was reduced  
4 as the pH increased. In addition, part of the supplied ozone may also be involved in parallel  
5 reactions on the surface of CNT, which is not accessible to MO molecules at high pH due to  
6 repulsion between MO and the CNT surface, leads to reduction in the rate constant of MO  
7 decolourisation in comparison to ozone alone as observed in Figure 7 when  $\text{pH} > 4$ .

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9

### 10 **Figure 7**

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#### 13 ***Effect of radical scavenger***

14 *Tert*-butanol, carbonate/bicarbonate and low pH (i.e. addition of  $\text{H}_3\text{O}^+$ ) are the most well-  
15 known and commonly used hydroxyl radical ( $\cdot\text{OH}$ ) scavengers, which all have strong effect  
16 on the pathway of ozone reactions (Hoigne et al., 1985; Gottschalk et al., 2000). The  
17 presence of a radical scavenger in the solution inhibits the radical pathway by quenching the  
18 chain reaction which inhibits further formation of hydroxyl radicals and only the molecular  
19 ozone reaction pathway (also known as the direct pathway) prevails in the solution. Hydroxyl  
20 radicals act as promoters of the chain reaction. The alcohol *tert*-butanol has been found to  
21 alter of the ozone mass transfer (Tizaoui et al., 2009), hence its use as a radical scavenger  
22 makes a direct comparison between with and without radical scavenger difficult. At high pH,  
23 the use of carbonate/bicarbonate is hence more plausible; their reaction rate constants with  
24  $\cdot\text{OH}$  radicals are  $3.9 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$  and  $8.5 \times 10^6 \text{ M}^{-1} \cdot \text{s}^{-1}$  for carbonate and bicarbonate  
25 respectively (Sonntag and von Gunten, 2012). Sodium bicarbonate at 0.2 mol/L was used in  
26 this study as  $\cdot\text{OH}$  scavenging agent in the presence of CNTs at 10 mg/L. The observed rate  
27 constants of the MO decolourisation reaction at pH 3 and pH7 in the presence of

1 bicarbonate are shown in Table 5. It can be calculated from Table 5 that the addition of  
2 bicarbonate has reduced  $k_{obs}$  by small percentages; 8% and 16% at pH 3 and 7 respectively.  
3 Since at pH 3 bicarbonate becomes carbonic acid, which has negligible  $\cdot\text{OH}$  scavenging  
4 effect, the small reduction in  $k_{obs}$  at pH 3 may be due only to experimental errors. The results  
5 suggest that overall the contribution of hydroxyl radicals to the decolourisation of MO is  
6 minimal and the main reaction pathway by which MO decolourises is molecular ozone.  
7 According to Table 4, the addition of 10 mg/L CNT at pH 3, increased  $k_{obs}$  by about 22%  
8 from that of ozone alone. It can hence be suggested that the increased  $k_{obs}$  in the presence  
9 of CNT at pH 3 was due mainly to a heterogeneous catalytic phenomenon by which CNT  
10 attracted both ozone and MO to its surface where the reaction took place (Beltran et al.,  
11 2002). Hassan and Hawkyard (2006) have also concluded that catalytic ozone  
12 decomposition by activated carbon improved colour decolourisation of dyes. Given that the  
13 hydroxyl radical scavenger had minimal effect, it can therefore be concluded that the  
14 decolourisation of MO with  $\text{O}_3/\text{CNT}$  is mainly due to molecular ozone reaction and the CNT  
15 plays an important role in enhancing the reaction rate only when the operating conditions are  
16 favourable for MO attraction to the CNT surface (i.e. pH 3).

17

18

19

**Table 5**

20

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### 22 ***Comparison between CNT and activated carbon***

23 A comparison between CNT and activated carbon (AC) was made in this study using a dose  
24 of 10 mg/L of each catalyst. The decolourisation rate in the presence of AC was also  
25 modelled by a pseudo first order kinetics (Mansouri et al., 2013) and the observed rate  
26 constants are presented in Table 6 for each case. At pH 3, the addition of AC improved  $k_{obs}$   
27 by approximately 3% whilst the addition of CNT increased  $k_{obs}$  by 22% as compared to  $k_{obs}$

1 obtained when ozone alone was used. This indicates that on a mass basis CNT improved  
2 the MO decolourisation by about 7 times more than AC. Larger doses of AC are then  
3 required to achieve MO decolourisation comparable to that obtained by CNT. It can therefore  
4 be suggested that CNT-based heterogeneous catalytic ozonation offers an efficient  
5 alternative for wastewater treatment.

6

7

8

### Table 6

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### 11 Conclusions

12 The removal of methyl orange (MO) using ozone in the presence and absence of multi-  
13 walled carbon nanotubes (CNTs) was studied in this research under different operating  
14 conditions. The operating conditions were initial concentration of MO, initial concentration of  
15 ozone, pH, radical scavenger, catalyst dosage and AC. The most effective improvements on  
16 the MO decolourisation were observed when CNT was used at pH 3 and at increased ozone  
17 concentration and CNT doses. An inlet ozone gas concentration of 6 g/m<sup>3</sup> NTP seems  
18 optimal since higher inlet concentrations resulted in insignificant change of the  
19 decolourisation rates. Molecular ozone reaction was found to dominate the pathway by  
20 which MO decolourisation occurred in solution and the contribution of •OH was suggested as  
21 minimal. The CNT was found to play an important role in enhancing the reaction rate only  
22 when the operating conditions are favourable for surface attraction of the MO molecule by  
23 CNT surface and this when pH=3. Higher pH values than 3 resulted in reduction of the  
24 decolourisation rates, possibly due to loss of part of the supplied ozone in parallel reactions  
25 of insignificant importance to the decolourisation of MO. Comparing activated carbon to  
26 CNTs, it was found that at the same dose, CNTs enhanced the decolourisation rates by

1 approximately 7 times more than AC relative to ozone alone. The study suggests that  
2 O<sub>3</sub>/CNTs can be used as an effective treatment system for wastewaters.

3

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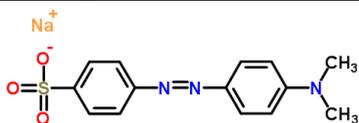
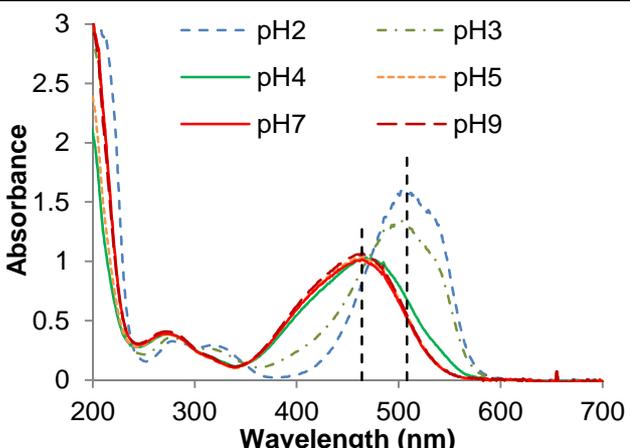
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## Tables

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**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 <sub>14</sub> H <sub>14</sub> N <sub>3</sub> NaO <sub>3</sub> S
Molecular mass	327.34 g/mol
Molecular structure	
pKa	3.47
Spectra at different pH #	
$\lambda_{\max}$	464 nm at pH $\geq 4$ # 508 nm at pH < 4 #
Extinction coefficient, $\epsilon$	23,362 $\pm$ 1% L.mol <sup>-1</sup> .cm <sup>-1</sup> at pH $\geq 4$ # 30,000-35,000 L.mol <sup>-1</sup> .cm <sup>-1</sup> at pH < 4 #
Colour	Yellow orange in alkaline medium and red in acid medium.
Uses	Textile industry, indicator in acid-base titrations.

4 #: determined in this study

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1 **Table 2:** Properties of the carbon nanotubes and activated carbon

Property	Value
<b>Carbon Nanotubes</b>	
Carbon Content (%)	96
Outer Diameter (nm)	~13-16
Length (μm)	~1
Aspect ratio (length/diameter)	~69
Bulk Density (g/cm <sup>3</sup> )	~0.19
Oxygen Content (%)	3.5 – 4
BET surface area (m <sup>2</sup> /g)	~250
<b>Activated Carbon</b>	
Particle size (mm)	~1.5
BET surface area (m <sup>2</sup> /g)	933
Average pore radius (Å)	11.6
specific pore volume (cm <sup>3</sup> /g)	0.54
pH <sub>pzc</sub>	10.68

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6 **Table 3:** Observed pseudo-first order reaction rate constant (T=23°C, pH=3, initial MO  
7 concentration C<sub>0</sub>=20 mg/L).

C <sub>O3</sub> (g/m <sup>3</sup> NTP)	k <sub>obs</sub> (min <sup>-1</sup> )
0	0.000
2	0.54
4	0.627
6	0.960
8	0.962

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13 **Table 4:** Effect of CNT dose on the observed first-order reaction rate constant (ozone  
14 concentration= 2 g/m<sup>3</sup> NTP, pH= 3, C<sub>0</sub>= 20 mg/L)

CNT dose (mg/L)	k <sub>obs</sub> (min <sup>-1</sup> )	R <sup>2</sup>
0	0.54	0.981
10	0.65	0.990
20	0.79	0.986
50	1.04	0.998

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1 **Table 5:** Effect of hydroxyl radical scavenger (bicarbonate) on the observed first-order  
 2 reaction rate constant (ozone gas concentration= 2 g/m<sup>3</sup>, pH= 3 and 7, C<sub>0</sub>= 20 mg/L, CNT =  
 3 10 mg/L)

<b><i>k<sub>obs</sub></i> at pH 3 (min<sup>-1</sup>)</b>		<b><i>k<sub>obs</sub></i> at pH 7 (min<sup>-1</sup>)</b>	
Without bicarbonate	0.65	Without bicarbonate	0.39
With bicarbonate	0.60	With bicarbonate	0.33

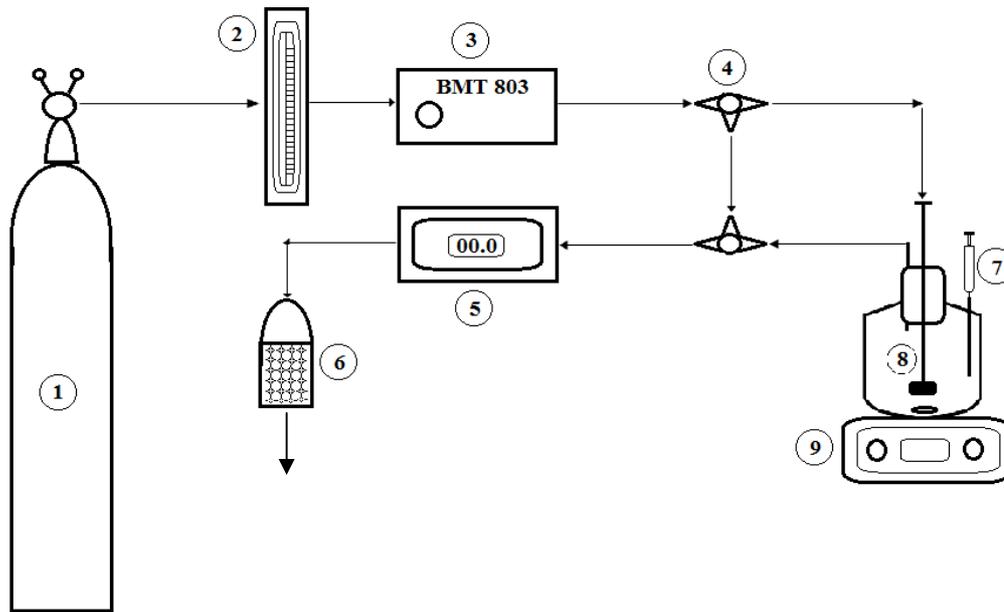
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13 **Table 6:** Comparison between CNT and AC as catalysts in heterogeneous catalytic  
 14 ozonation (ozone gas concentration= 2 g/m<sup>3</sup>, C<sub>0</sub>= 20 mg/L, pH=3, CNT dose = 10 mg/L, AC  
 15 dose = 10 mg/L)

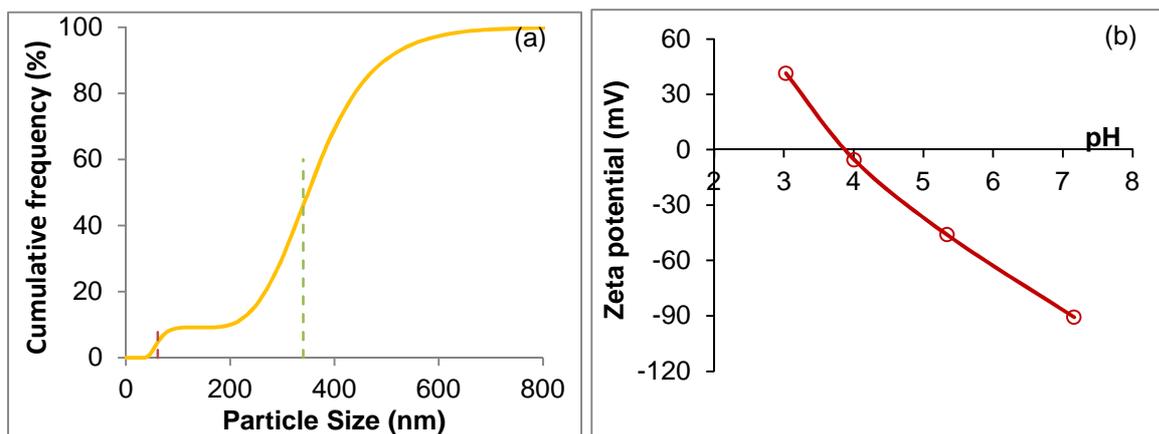
<b>System</b>	<b><i>K<sub>obs</sub></i> (min<sup>-1</sup>)</b>
O <sub>3</sub> alone	0.54
O <sub>3</sub> /AC	0.56
O <sub>3</sub> /CNT	0.65

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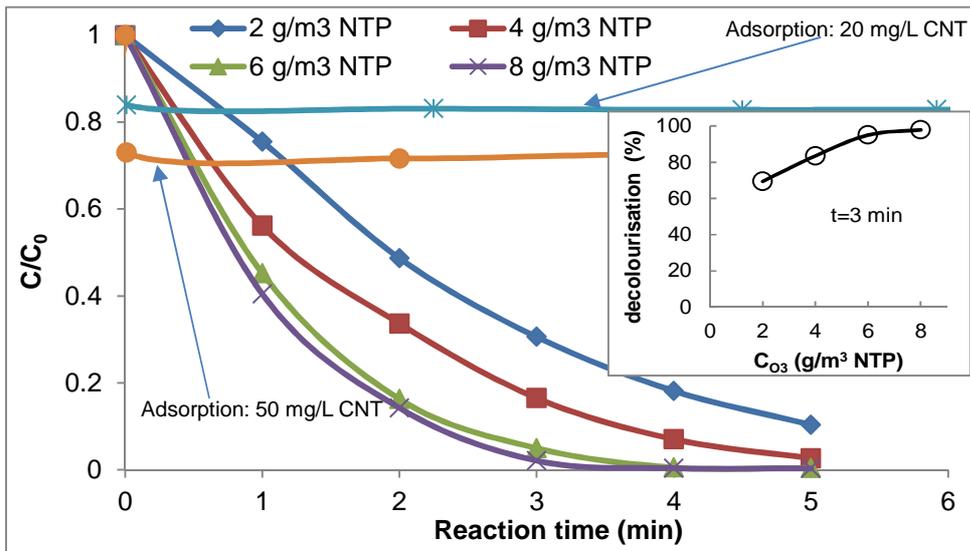
## Figures



**Figure 1:** Experimental setup: 1- Oxygen cylinder, 2- Gas flow meter, 3- Ozone generator, 4- Three-way valve, 5- Ozone analyser, 6- Ozone destructor, 7- Sampling syringe, 8- Gas diffuser, 9- Magnetic stirrer.



**Figure 2:** CNT characterisation (a) cumulative particle size distribution; (b) zeta potential as function of pH



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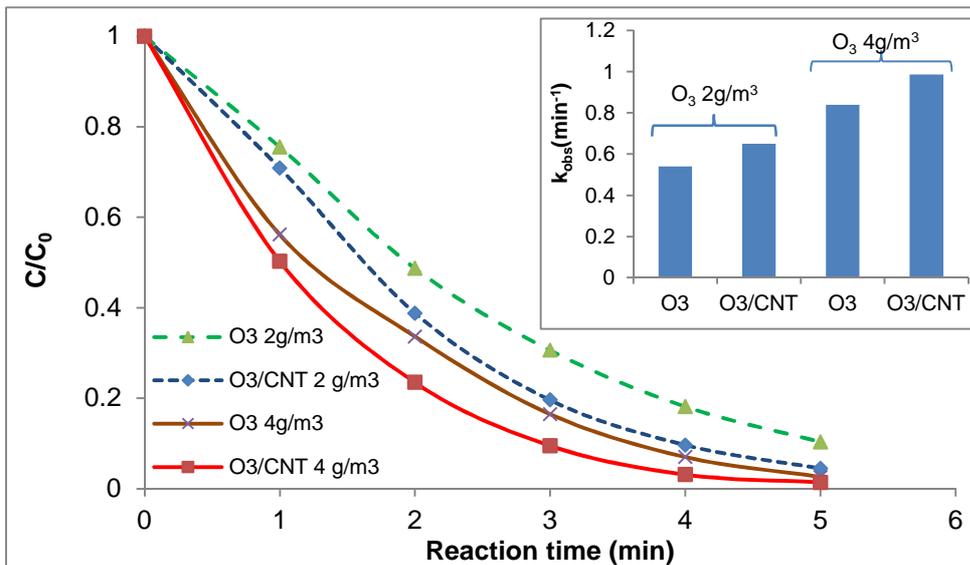
2 **Figure 3:** Removal of MO by adsorption alone on CNTs and by ozone alone at different  
 3 concentrations ( $T=23\pm 1^\circ\text{C}$ ,  $\text{pH}=3$ ,  $C_0=20$  mg/L).

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9 **Figure 4:** Effect of initial ozone concentration on MO decolourisation (volume= 150 mL,  $C_0=$   
 10 20 mg/L, gas flow rate= 0.4 L/min, CNT = 10 mg/L when used,  $\text{pH}= 3$  and temperature=  
 11  $23\pm 1^\circ\text{C}$ ).

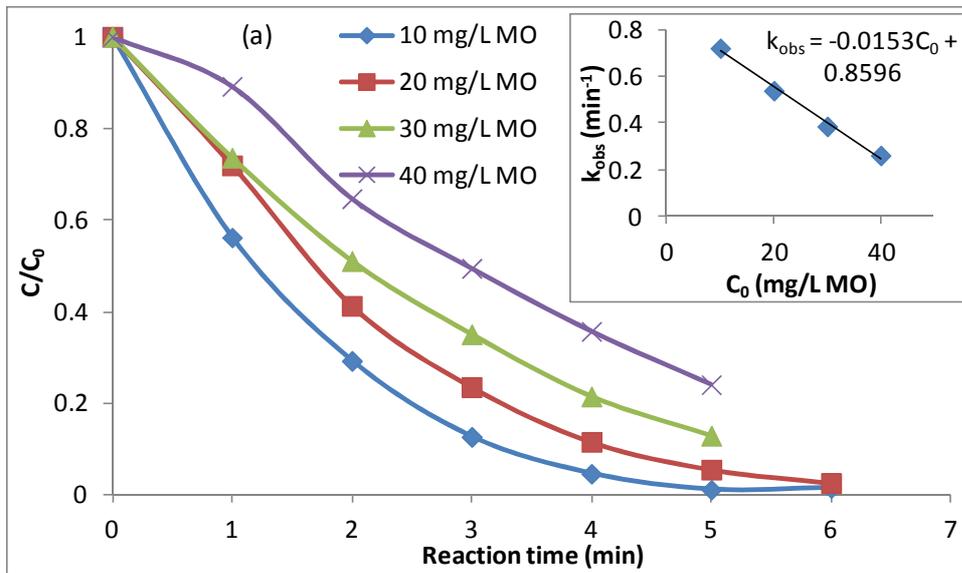
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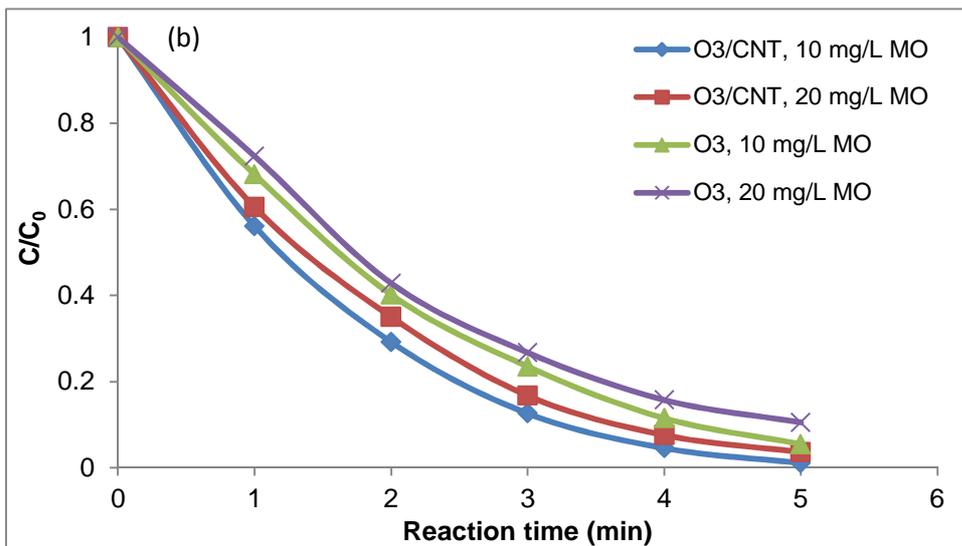
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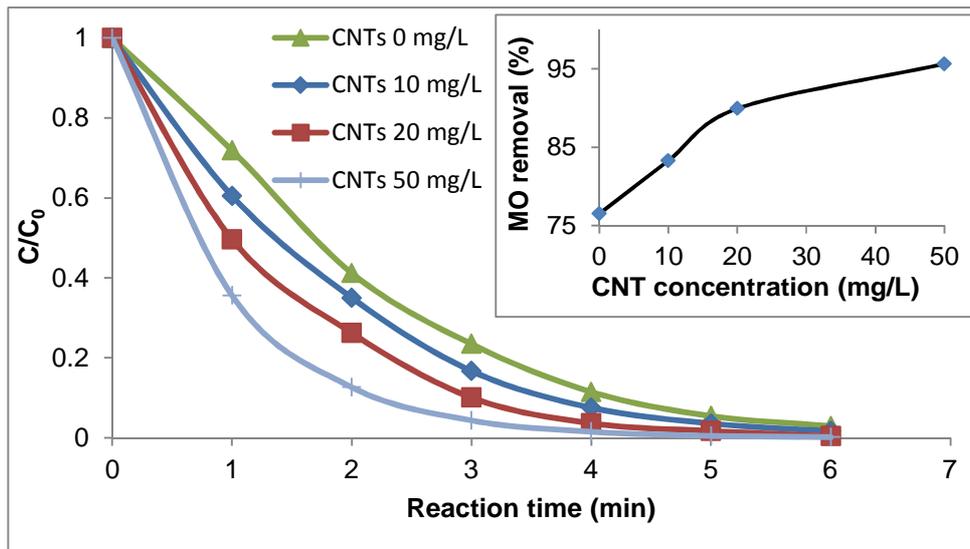
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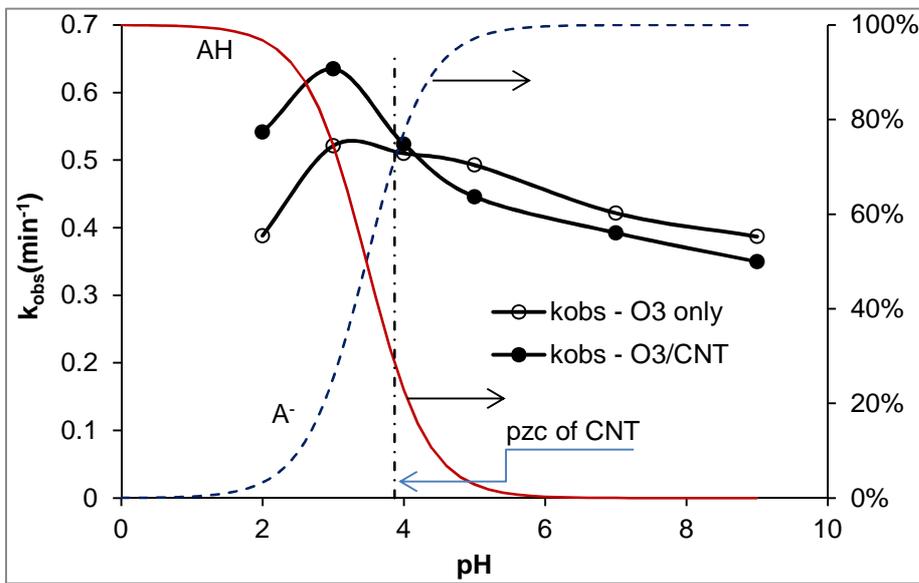
5 **Figure 5:** Effect of MO concentration on solution decolourisation (a) ozone only (b)  
6 comparison between  $O_3$  and  $O_3/CNT$  ( $O_3$  gas concentration 2 g/m<sup>3</sup> NTP, gas flow rate 0.4  
7 L/min, pH= 3, volume= 150 mL, temperature= 23±1 °C, CNT= 10 mg/L).

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**Figure 6:** MO removal at different CNT concentrations; inset: removal percentages at reaction time of 3 min (ozone concentration= 2 g/m<sup>3</sup> NTP, pH= 3, C<sub>0</sub>=20 mg/L)



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**Figure 7:** Effect of pH on the observed first-order reaction rate constant (ozone concentration= 2 g/m<sup>3</sup>, C<sub>0</sub>= 20 mg/L, CNT = 10 mg/L)