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## COMPARISON ON SOLAR PHOTOCATALYTIC DEGRADATION OF ORANGE G AND NEW COCCINE USING ZINC OXIDE AS CATALYST

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### Abstract

The mineralization of azo dyes could be realized through solar photocatalytic degradation that is a green method where non-harmful end products are produced. The aim of this study was to investigate the mineralization of Orange G (OG) and New Coccine (NC) using ZnO as catalyst. The degradation of the azo dyes was conducted at different experimental conditions, and parameters such as effect of sunlight to the degradation rate, initial azo dye concentration, amounts of catalyst dosage, pH and effect of aeration to the decolorization of azo dye were investigated. Photocatalytic mineralization of the azo dyes was evaluated through the analysis of UV-Vis spectra, chemical oxygen demand (COD) and ion chromatography (IC) for residual ionic species analysis. The results showed that solar photocatalytic degradation using ZnO was effective for colour removal and the photodegradation rate followed Langmuir-Hinshelwood kinetic model. It was observed that the degradation rate of NC was higher than OG which may be due to the different number of sulphonate ions that are attached on to the azo dye molecule.

*Key words:* new coccine, orange G, solar photocatalysis, sulphonate group, zinc oxide

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### 1. Introduction

Azo dyes are one of the oldest industrially synthesized organic compounds that are used as colouring agents for textile, ink, plastic, pulp and paper, glove and paint, and they represent the major group, 60-70% of the dyes that are currently manufactured (Brás et al., 2005; Omar, 2008). The presence of excessive azo dyes and the formation of the intermediate products from the reduction of the azo bond into water streams could be harmful to humans and toxic to aquatic life and it also will give negative aesthetic effects to the environment (Brás et al., 2005).

There are various treatment techniques employed for removing azo dyes such as adsorption,

filtration, coagulation and flocculation, and biological processes (Brás et al., 2005; Omar, 2008; Sánchez-Duarte et al., 2016). The disadvantage of these treatment techniques is that they only promote the transfer of the waste from liquid phase to the solid phase. Nowadays, photocatalytic techniques have become one of the most promising processes for treating azo dyes as these techniques could mineralize the azo dyes into carbon dioxide and water which are non-harmful end products. Photocatalytic techniques mediated by solar irradiation steam great interest because it is inexhaustible and free (Ho et al., 2012). Among various semiconductor photocatalytic materials such as TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, CdO and CuO, zinc oxide (ZnO) occupies a special place due to its photosensitive

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nature, wide band gap (3.2 eV) and non-toxicity (Kajbafvala et al., 2012). One of the advantages of ZnO compared to TiO<sub>2</sub> is it can absorb over a larger fraction of the solar spectrum (Jafari et al., 2016; Pardeshi and Patil, 2009). Lu et al. (2009) used ZnO to degrade Basic Blue II under visible light irradiation and studied the effects of important operating parameters like initial concentration, initial pH and catalyst dosage. Photocatalytic process occurs based on the generation of electron-hole pairs as the photocatalyst is irradiated with light irradiation higher than their band gap (Jiang et al., 2008). The mechanism of photocatalytic process is described as when photo-excitation with light of energy greater than the band gap of ZnO, it will promote an electron from the valence band to the conduction band and leaves a hole pair in the valence band. Holes that generated on the surface of the material react with water, hydroxide ions and oxygen to form hydroxyl radicals, which react with the pollutants leading to their degradation (Narayan et al., 2009).

The objective of the present study was to investigate some process variables on the mineralization of two azo dyes (Orange G and New Coccine) such as sunlight radiation, initial dye concentration, catalyst dosage, pH of the dye and existence of aeration system. The data obtained were analysed with the Langmuir-Hinshelwood kinetic model. Although there are some reports on the degradation of azo dyes using ZnO as a catalyst, however, only few of them were conducted for Orange G (OG) and New Coccine (NC). The photodegradation rate between of the two azo dyes was compared and discussed based on the molecular structure of the azo dyes.

## 2. Materials and method

### 2.1. Chemical

Two monoazo dyes which are Orange G and New Coccine with the molecular formula, C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>7</sub>S<sub>2</sub> and C<sub>20</sub>H<sub>11</sub>N<sub>2</sub>Na<sub>3</sub>O<sub>10</sub>S<sub>3</sub>, respectively, were used in this study. The molecular weights of OG and NC are 425.27 g/mol and 604.47 g/mol, respectively. The chemical structure of both dyes is shown in Fig. 1. Both of dyes and zinc oxide (ZnO) were supplied by Sigma Aldrich and HmbG, respectively. The molecular weight of ZnO is 81.37 g/mol and its particle size is 140 – 480 nm. All chemicals were of analytical grade and used without further purification.

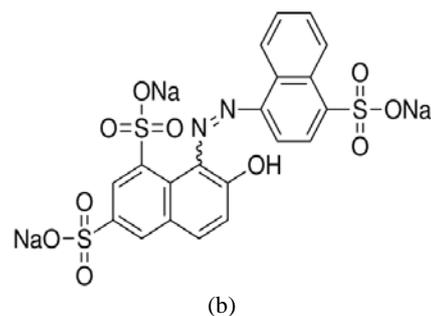
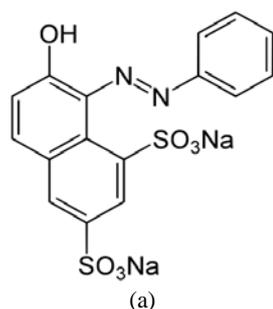


Fig. 1. Molecular structure of (a) Orange G and (b) New Coccine

### 2.2. Photocatalytic procedure

The stock solutions for both dyes were prepared in 1.0 g/L concentrations. The photocatalytic degradation of the azo dyes was conducted in 1000 mL beakers, well mixed with magnetic stirrer and placed under direct solar light. An appropriate amount of azo dyes from stock solution was diluted to 500 mL with ultrapure water for each experiment. The photocatalytic process was conducted in batch reactor for 5 hours and about 15 mL of water sample was collected from the beakers with a syringe at 0, 0.5, 1, 1.5, 2, 3, 4 and 5 hours after irradiated with solar light. In order to study the effect of ZnO dosage, its dosage varied to 0.05 g, 0.10 g, 0.15 g, 0.20 g and 0.25 g. The air diffuser was used to supply aeration into 100 mg/L of azo dye solutions with 0.1 g of ZnO in order to evaluate the effect of aeration on the photocatalytic rate of OG and NC. The water samples then were filtered through filter paper which its size is 125 mm to remove ZnO particles. The clear water samples were analysed to determine the concentration of OG and NC by UV-Vis Spectrophotometer (Hitachi U-2800, Japan). The maximum absorbance wavelength ( $\lambda_{max}$ ) of OG and NC was found at 512 and 536 nm, respectively.

The mineralization of dyes was monitored through changes in UV-Vis spectra, ion-chromatography and chemical oxygen demand (COD). The samples were filtered through filter papers and then analysed for COD, using HACH DR2800 spectrophotometer. The concentration of SO<sub>4</sub><sup>2-</sup> of both dyes was determined by ion chromatography system (ICS-100, Dionex).

## 3. Results and discussion

### 3.1. Effect of solar light irradiation

In order to evaluate the effects of solar light irradiation on the degradation of OG and NC, two sets of experiment were run simultaneously, one set was exposed to the solar light and the other one was conducted in the absence of solar light, which the beaker was fully covered with aluminium foil. Figure 2 shows the degradation of OG and NC with and without solar light irradiation. The concentration of

both azo dyes, OG and NC, decreased with solar light irradiation compared to dyes which degradation was conducted in the laboratory (without solar light irradiation). It was observed that the removal efficiency of OG and NC was 90.6 % and 93.6 %, respectively, after the azo dye solutions were exposed to solar light irradiation for 5 hours in the presence of 0.1 g ZnO. On the other hand, minimal dye removal was observed in the case without solar light irradiation which could be due to the adsorption of dye molecules onto surface of ZnO (Thennarasu et al., 2012). The catalyst powder cannot promote the oxidation of dye in the absence of light irradiation (Sakthivel et al., 2003).

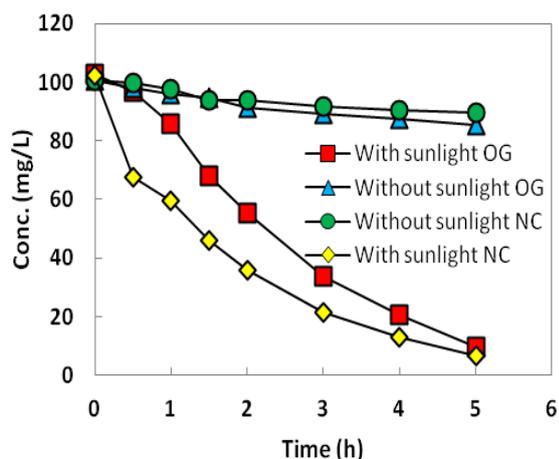


Fig. 2. Photocatalytic degradation of Orange G and New Coccine with and without solar light irradiation (Initial dye concentration = 100 mg/L, ZnO dosage = 0.1 g)

### 3.2. Effect of initial dye concentration

The effect of initial concentration of OG and NC on the rate of degradation was studied by varying the initial dye concentration of 10, 30, 50, 80 and 100 mg/L with 0.1 g of ZnO dosage. The removal efficiency for both azo dyes decreased with the increase of dye concentration. As shown in Fig. 3(a) and (b), complete decolorization was found in the 50 mg/L of OG within 3 hours of solar light irradiation whereas decolorization of NC was achieved within 2 hours for the same concentration. The percentage removal of OG and NC at 5 hour with highest tested concentration, 100 mg/L, was 93.6 % and 97.3 %, respectively.

The probability of •OH radical formation on the surface of photocatalyst and the probability of the radicals react with the azo dye molecule may contribute to the degradation rate of the azo dyes (Konstantinou and Albanis, 2004). As the concentration of the azo dyes increased in the solution, it will reduce the amount of photons entering the dye solutions and absorbed by the photocatalyst to form the •OH radical and subsequently decrease the photocatalytic degradation rate. Meanwhile, the reverse effect was observed in the low azo dye concentration (Kansal et al., 2007). Muruganandham et al. (2006) observed the same

trend in the photocatalytic degradation of Reactive Black 5 (RB 5) using TiO<sub>2</sub> as catalyst. Moreover, the number of sulphonate group has an impact on the degradation of dyes. As the number of sulphonate group increased in the azo dye molecules, it will increase the adsorption capacity of the dye molecules onto the catalyst (Khataee et al., 2009). This study shows that the degradation NC was faster compared to the OG which may be ascribed to the different number of sulphonate group attached to the azo dye molecules. The NC and OG have 3 and 2 sulphonate group, respectively. Higher number of sulphonate groups will contribute to the greater adsorption capacity of the dye molecule onto the surface of ZnO and subsequently perform better in the degradation by the •OH radical. This is in agreement with the result which reported by Khataee et al. (2009).

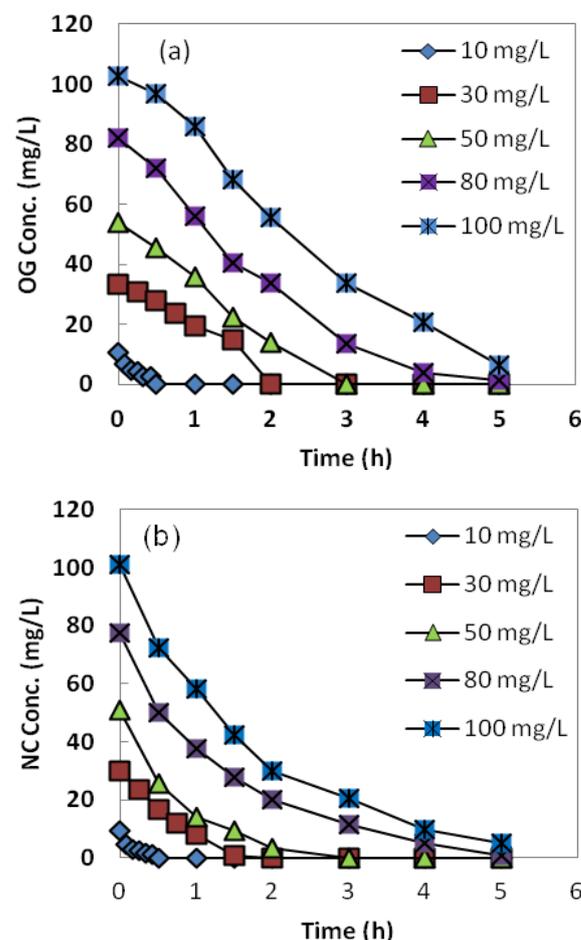


Fig. 3. Photocatalytic degradation of (a) Orange G and (b) New Coccine with different initial azo dye concentrations (ZnO dosage = 0.1 g)

Jiang et al. (2008) suggested that heterogeneous photocatalytic decolorization and the degradation of dyes can be described by Langmuir-Hinshelwood kinetic model as shown below (Eq. 1):

$$Rate = - (dC/dt) = kKC / (1 + KC) \quad (1)$$

where: *C* the concentration of azo dye (mg/L), *t* the irradiation time, *k* the reaction rate constant (mg/L. h)

and  $K$  the adsorption coefficient of the dye onto the photocatalyst particle (L/mg). At low concentrations of dyes ( $KC \ll 1$ ), value of  $KC$  can be neglected. The equation can be simplified to the pseudo-first-order kinetic model equation (Gupta et al., 2007) (Eq. 2).

$$\ln(C_0/C) = kKt = k_{app} \cdot t \quad (2)$$

When a plot of  $\ln(C_0/C)$  versus time results in a straight line, the pseudo-first-order decolorization rate constant ( $k_{app}$ ) can be obtained from the slope of the graph.  $k_{app}$  the apparent rate constant calculated from the curves ( $h^{-1}$ ).

The data obtained from photocatalytic degradation of OG and NC followed the Langmuir-Hinshelwood kinetic model. As shown in Table 1, the pseudo-first-order rate constant for both azo dyes decreased as the initial concentration of dyes increased. Based on the  $k$  value, it showed that better performance occurred at the lower concentration of the azo dyes compared to higher concentration. From the table, it also can be seen that NC has higher rate constant compared to that of OG and it was observed that NC was easier and faster to be degraded than OG.

**Table 1.**  $k_{app}$  and  $R^2$  for OG and NC at different initial concentration

$C_0$ (mg/L)	$k_{app}$ ( $h^{-1}$ )		$R^2$	
	OG	NC	OG	NC
10	3.729	5.13	0.955	0.918
30	1.115	1.256	0.981	0.992
50	0.599	1.266	0.936	0.987
80	0.712	0.667	0.936	0.995
100	0.445	0.614	0.906	0.974

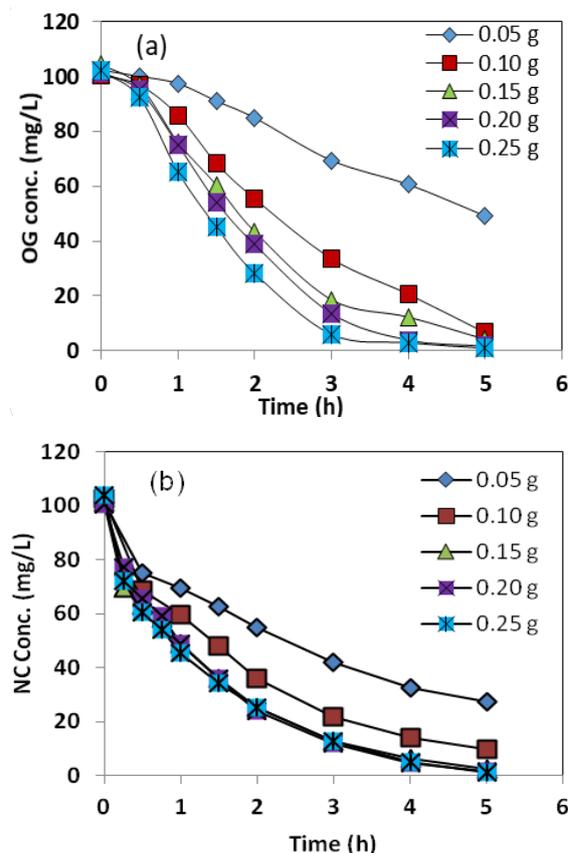
### 3.3. Effect of ZnO dosage

The influence of catalyst dosage, 0.05, 0.10, 0.15, 0.20 and 0.25 g, on the photodegradation of OG and NC was evaluated in this study. As shown in Fig. 4, the azo dyes were degraded rapidly as the dosage of ZnO increase. Both of dyes in the same concentration took 5 hours to completely degrade at a highest catalyst dosage (0.25 g). This could be explained by increasing the amount of catalyst, it will increase the amount of active sites that are available on the catalyst surface for the reaction (Peng et al., 2013). However, some of the researchers observed reverse trend at higher dosages of photocatalyst due to the scattered of the light and reduction of the light penetration into solutions and subsequently the formation of  $\bullet OH$  radical will be affected (Sohrabi and Ghavami, 2010). This finding of the current study is consistent with those of Wang et al. (2008) who found decolorization rate of Basic Violet 10 achieved a maximum at a dosage of 5333 ppm and then decreased with increase in catalyst dosage.

### 3.4. Effect of pH

The effect of pH on the degradation of both azo dyes was studied with a constant concentration in

pH 1, 3, 5, 9 and 11. The pH for the both aqueous phase was adjusted using 1 M of  $H_2SO_4$  and NaOH. As shown in Fig. 5, the degradation rate for both azo dyes was higher in alkaline solution compared to acidic solution.



**Fig. 4.** Photocatalytic degradation of (a) Orange G and (b) New Coccine with different dosage of ZnO (Initial dye concentration = 100 mg/L)

The optimum degradation rate was achieved as the pH of the azo dye solution increased up to 11. Photocatalytic degradation of OG and NC could not be investigated at pH 1 since the catalyst dissolved in the presence of highly acidic solution (Ameta et al., 2004). There are two reasons that can describe these phenomena (Fabbri et al., 2006; Giwa et al., 2012; Qamar et al., 2005). The agglomeration of ZnO particles at lower pH may cause the reduction in the adsorption of dye molecule onto the surface of photocatalyst and the absorption of photon also will be affected as well. Furthermore, the azo bond ( $-N=N-$ ) is particularly susceptible to electrophilic attack by  $\bullet OH$  radicals and the excessive of  $H^+$  ions at lower pH may interact with azo bond and subsequently decreases the densities of electron at azo bond. The zero point charge ( $pH_{zpc}$ ) of ZnO also plays an important role in this study and its  $pH_{zpc}$  is 9.0 (Peng et al., 2013). ZnO surface is positively charged at below its  $pH_{zpc}$  (Thennarasu et al., 2012). The degradation rate of OG and NC increases in basic pHs phase because this phase favours the formation of more  $\bullet OH$  radicals due to the presence of a large quantity of  $OH^-$  ions in alkaline phase

(Sakthivel et al., 2003). This result is consistent with Wang et al. (2007) which found that fast increase in the degradation of methyl orange with the increase of the pH value.

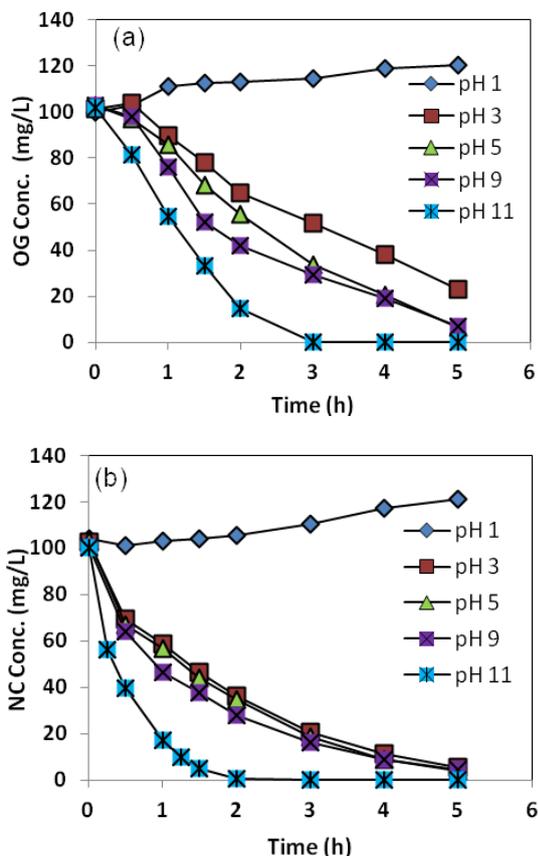


Fig. 5. Photocatalytic degradation of (a) Orange G and (b) New Coccine with different pH (Initial dye concentration = 100 mg/L, ZnO dosage = 0.1 g)

### 3.5. Effect of aeration

Introducing aeration during the photocatalytic reaction, will enhance the decolorization of the azo dyes (Abo-Farha, 2010). As shown in Fig. 6, it shows that the decolorization of both azo dyes was performed better in the aerated condition compared to the non-aerated ones. Besides, it also shows that NC was decolorised more quickly compared to OG. The oxygen molecules that were supplied into the dye solution could act as an electron acceptor and this will minimize the electron-hole pair recombination (Litter, 1999). The recombination of electron-hole pair will affect the formation of  $\bullet\text{OH}$  radicals. The received of the oxygen molecule by the conduction band may enhance the formation of superoxide radical anion which increases the degradation rate (Qamar and Muneer, 2009).

### 3.6. Mineralization of dye

#### 3.6.1. Wavelength scan

The mineralization of the azo dyes using a solar photocatalytic process was evaluated with UV-Vis analysis and the changes in the absorption

spectra of OG and NC for the concentration of 50 mg/L at different irradiation times are shown in Fig. 7.

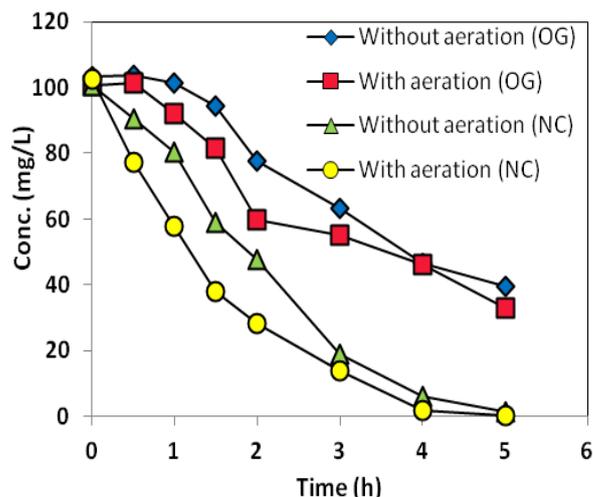


Fig. 6. Photocatalytic degradation of Orange G and New Coccine with and without aeration (Initial dye concentration = 100 mg/L, ZnO dosage = 0.1 g)

The adsorption peaks in visible or UV regions of spectra for both dyes rapidly decreased as the time of solar light irradiation time increase. It can be seen that there are three absorbance peaks that present in the spectrum of OG (215, 320 and 480 nm), whereas two absorbance peaks for NC (329 and 500 nm). The absorbance peak in the visible region at 480 nm and 500 nm, for OG and NC, respectively referred to the azo bond ( $-\text{N}=\text{N}-$ ) which cause the colour of the dyes. On the other hand, the absorbance peak in the UV region indicated the aromatic compound that present in dye molecules such as a benzene ring (200 – 300 nm) and naphthalene ring (300 – 400 nm) (Khatee et al., 2009). The cleavage of azo bonds that responsible for the characteristic colour of OG and NC caused the decolorization of both dyes (Thenarasu et al., 2012).

The molecular structure of azo dye may affect the degradation rate through the photocatalytic process. Tang et al. (1997) reported the two naphthalene rings in the New Coccine could cause a steric hindrance to the azo group to form coordinate bonding to  $\text{TiO}_2$  and thus the cleavage of azo dyes was affected. The adsorption peaks of both azo dyes reduced to the base line of the spectra after 4 h of solar light irradiation, which indicated that the azo bond could be destroyed which led to the decolorization and the benzene and naphthalene groups may be fully or partially being mineralized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Guettaï and Amar, 2005).

#### 3.6.2. Chemical Oxygen Demand (COD)

The degree of the mineralization of photocatalytic processes could be measured by the total amount of organic matters present in the solution after the treatment process (Stylidi et al., 2003). Thus, COD monitoring is another method that

can be employed to determine the mineralization of azo dyes through the photocatalytic process. As shown in Fig. 8, both of the dyes with 10 mg/L were mineralized completely within 5 hours, while OG with concentration 50 mg/L and 100 mg/L not achieve complete mineralization as well as NC at concentration 100 mg/L.

The incomplete removal of COD for both azo dyes at certain concentrations could be due to the formation of intermediate products after the cleavage of azo bonds and breakdown of naphthalene and benzene rings. The intermediate products could contribute to the COD level in the solution (Stylidi et al., 2003). Tanaka et al. (2000) reported that the intermediate products for OG were phenol and hydroquinone, while for NC, its intermediate products were formic acid, acetic acid, glycolic acid, glyoxylic acid and malonic acid. The formation of these acids suggests the mineralization of the benzene and naphthalene groups after the breakdown of azo bond through photocatalytic process (Tanaka et al., 2000).

### 3.6.3. Ion Chromatography (IC)

The concentration of sulphate ( $\text{SO}_4^{2-}$ ) ions in OG and NC solutions were determined through ion chromatography. As shown in Fig. 9, it can be observed that all the azo dyes solutions contained  $\text{SO}_4^{2-}$  ion after the photocatalytic process and this indicated the breakdown of the bonding between the sulphonate group and the benzene or naphthalene groups. The concentration of  $\text{SO}_4^{2-}$  at 100 mg/L solutions was the highest, followed by 50 mg/L and lastly 10 mg/L. The result shows the mineralization of the azo dye through photocatalytic degradation by ZnO. The different number of sulphonate group also plays an important role in photocatalytic degradation. Generally, the concentration of  $\text{SO}_4^{2-}$  produced from the NC higher than OG solutions indicated the greater degradation rate on the NC compared to OG. The adsorption of the dye molecules on the catalyst was increased by increasing the number of sulphonate group (Muruganandham et al., 2006) due to the adsorption rate of NC was higher than OG and subsequently increase the degradation rate.

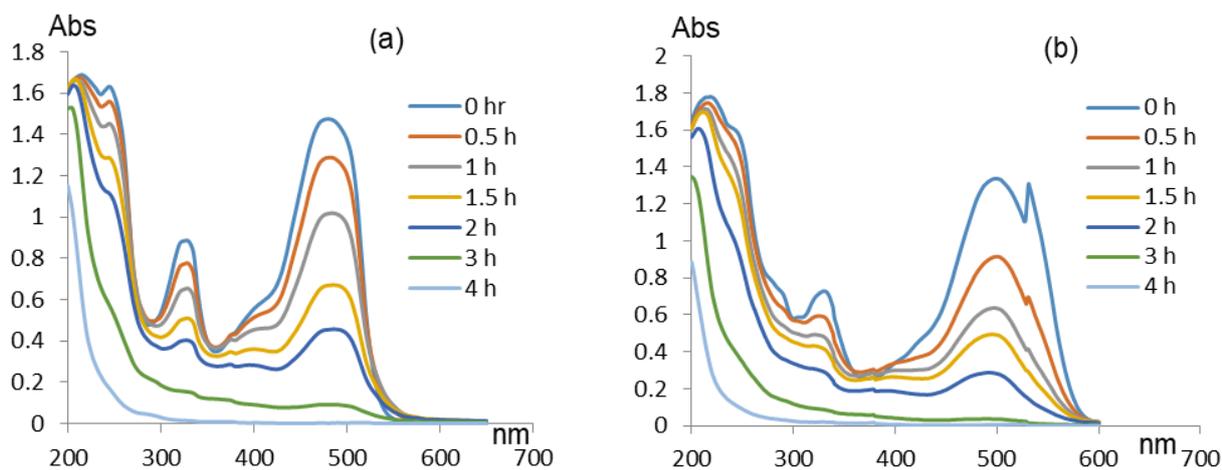


Fig. 7. UV-Vis analysis for (a) Orange G and (b) New Coccine (Dye concentration = 50 mg/L, ZnO dosage = 0.1 g)

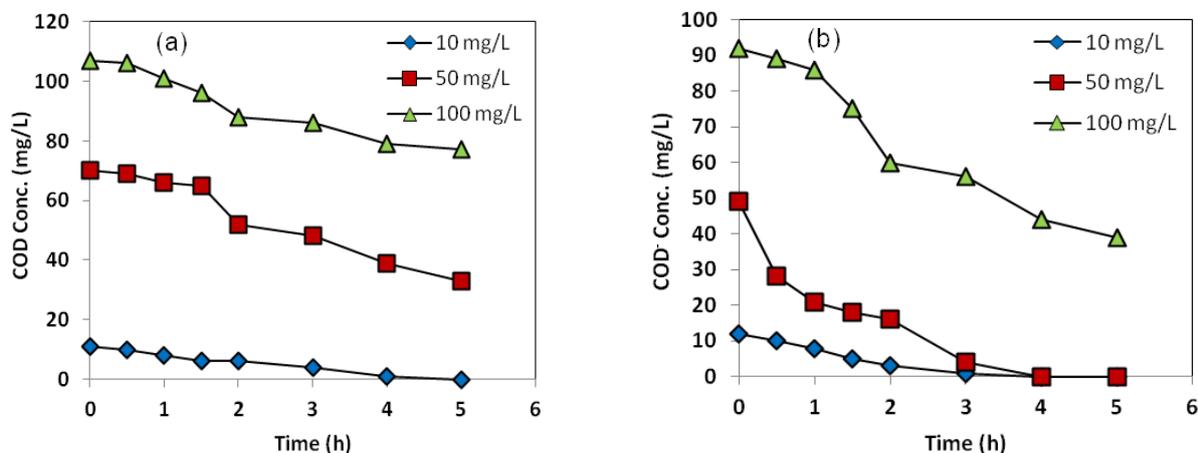


Fig. 8. COD monitoring in photocatalytic degradation of (a) Orange G and (b) New Coccine (ZnO dosage = 0.1 g)

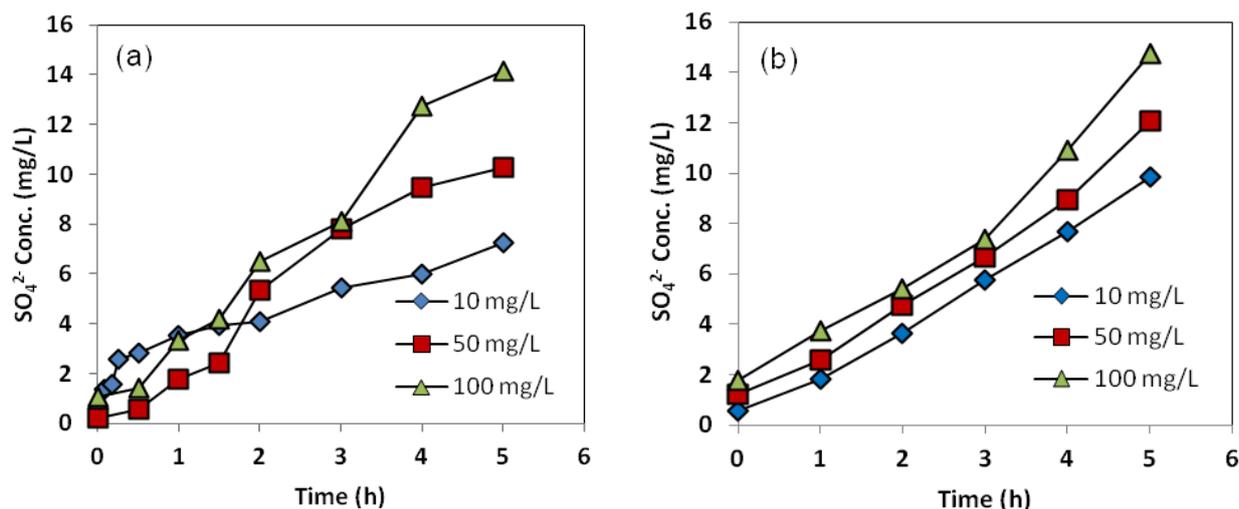


Fig. 9. IC analysis in photocatalytic degradation of (a) Orange G and (b) New Coccine (ZnO dosage = 0.1 g)

#### 4. Conclusions

The solar photocatalytic degradation of OG and NC was investigated and compared for some operational parameters using ZnO as catalyst. It was observed that the degradation rate of the azo dyes increased with the exposed to the solar light irradiation, low initial dye concentration, higher photocatalyst dosages, with aeration and high pH solution.

The photocatalytic degradation rate for both azo dyes followed Langmuir-Hinshelwood kinetic model and NC showed a higher degradation rate than OG which could be ascribed to the different number of sulphonate groups that attached to the azo dye molecule. Partial photocatalytic mineralization of the azo dyes was shown in the COD, UV-Vis and IC analysis.

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