Comparison of Cu^{2+} and Zn^{2+} thermalcatalyst in treating diazo dye

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Abstract. This research demonstrates the comparison between copper (II) sulphate ($CuSO_4$) and zinc oxide (ZnO) as thermalcatalysts in thermolysis process for the treatment of diazo reactive black 5 (RB 5) wastewater. $CuSO_4$ was found to be the most effective thermalcatalyst in comparison to ZnO. The color removal efficiency of RB 5 catalysed by $CuSO_4$ and ZnO were 91.55 % at pH 9.5 and 7.36 % at pH 2, respectively. From the UV-Vis wavelength scan, $CuSO_4$ catalyst is able to cleave the molecular structure bonding more efficiently compared to ZnO. ZnO which only show a slight decay on the main chemical network strands: azo bond, naphthalene and benzene rings whereas $CuSO_4$ catalyst is able to fragment azo bond and naphthalene more effectively. The degradation reactions of $CuSO_4$ and ZnO as thermalcatalysts in thermolysis process were compared.

1. Introduction

Industrial manufacturing factories, particularly those involved in colour finishing processes are major source of considerable pollution. Dominant industry contributed to the foulest contamination and pollutants is textile dye processing industries. In detail, textile industry is a group of related industries uses cotton, wool and synthetic fibers to produce fabric. Textile dyes are well known mutagens and carcinogens posing risks to various ecosystems, animals' health and agriculture. This is due to the recalcitrant nature of textile effluents which largely containing high concentrations of non-degradable dyestuffs. Presence of non-degradable dye molecule in water bodies decrease the dissemination of daylight, thus reducing the algae and other aquatic vegetation photosynthesis rate. Consequently, concentration of dissolved oxygen become lower causing wide array of toxic effects to the aquatic ecosystems and deteriorate the water quality level. Among the dye variations, the major concern of dye types are azo dyes and their derivatives which are mutagenic and carcinogenic. For instance, the complex structure of amino azo benzene dyes may lead to cancer [1]. On the other hands, reactive dyes are mostly used in dye manufacturing industry since reactive dyes are the most efficient dye to impart colour on the material. However, untreated reactive dyes are carcinogenic since it potentially boost the rate of bladder cancer [2]. In the view of these facts, treatment of detoxification and degradation of textile dyes and effluents is crucial. Development of sustainable technologies and techniques to control dye pollution such as adsorption [3], membrane filtration [4], photocatalytic [5], ozonation [6], sonophotocatalytic [7], ultrasound assisted Fenton [8] and microbial electrolysis [9] are generally employed for remediation of dye containing effluents [10]. Dye wastewater treatment by applying thermolysis process is a new insight and yet to be explored. In this research, thermolysis process catalysed by different catalysts, $CuSO_4$ and ZnO were applied in treating reactive diazo dye.

Reactive Black 5 (RB 5) was used as the dye model to study the performance of thermolysis process in treating diazo reactive typed dye. The extent of degradation of the main chemical network strands was investigated to evaluate the efficiency of thermolysis to treat the degradation intermediates.
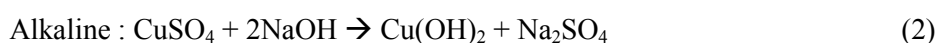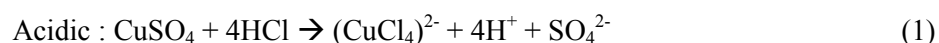
2. Material and methods

Reactive Black 5 (RB 5) with a molecular structure $C_{26}H_{21}N_5Na_4O_{19}S_6$ was supplied by Sigma-Aldrich. 1 g of RB 5 was diluted in 1L volumetric flask with distilled water in order to obtain 1000 ppm RB 5 stock solution. After that, 100 ppm of RB 5 solution was prepared by using dilution equation. Thermolysis experiments were carried out in a rotamantle. A vertical water-cooled condenser was attached to the reactor in order to prevent any loss of water vapour. Initially, pH of 250 ml of 100 ppm RB 5 solution was measured and adjusted by adding HCl or NaOH within the range in between pH 2 to 12. The solution was stirred and heated until the desired temperature before adding catalyst to the solutions. The catalysts used are copper (II) sulphate, $CuSO_4$ and zinc oxide, ZnO. In order to determine the optimum condition of thermolysis process in treating RB 5, Hitachi U-2810 UV-Visible scanning spectrophotometry were used to identify the transmission of absorption of ultraviolet light and visible light with a sample in the wavelength between 200 to 800 nm.

3. Results and discussion

3.1. Performance analysis of catalysis $CuSO_4$ and ZnO as thermalcatalyst

In thermolysis process, apart from temperature is the critical parameter affect the treatment performance, catalyst which is used to enhance the thermolysis process is essential as an auxiliary agent for the molecular structure bonding fragmentation [11]. Therefore, selection of catalyst was conducted by comparing the colour removal efficiency between $CuSO_4$ and ZnO as thermalcatalyst under effect of pH. By keeping constant parameter for temperature of 60 ℃, reaction time of an hour and catalyst mass loading of 0.5 g/L for effect evaluation on pH, which varied in the range of 2 – 12. Figure 1 depicts the color removal efficiency of RB 5 catalysed by $CuSO_4$ and ZnO with respect to pH. The maximum percentage of colour removal for $CuSO_4$ and ZnO were 91.55 % at pH 9.5 and 7.36 % at pH 2, respectively. For $CuSO_4$ catalyst, the colour removal efficiency increases rapidly from pH 2 to 9.5 and the removal efficiency start to decrease after pH 9.5. In acidic condition, copper ions tend to react with chlorine ions to form tetrachlorocuprate(II) ion ($(CuCl_4)^{2-}$), which readily react with RB 5. In alkaline condition, copper ions tends to form insoluble copper hydroxide ($Cu(OH)_2$) which support the low color removal of RB 5 beyond pH 9.5 [12]. The acidic and alkaline reaction of $CuSO_4$ as shown in equation (1) and (2).

$$\text{Acidic} : CuSO_4 + 4HCl \rightarrow (CuCl_4)^{2-} + 4H^+ + SO_4^{2-} \tag{1}$$

$$\text{Alkaline} : CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4 \tag{2}$$

On the other hand, ZnO only shows a removal of 7.36% at pH 2. According to Greenwood et al, (1997) ZnO will react with Cl- ions presence in the solution to form zinc chloride ($ZnCl_2$) in acidic solution [13]. Subsequently, ZnO hardly shown color removal efficiency throughout the pH ranges from 4 to 12 since zinc hydroxide ($Zn(OH)_2$) white precipitation is formed in alkaline condition.

Acidic : $ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$ (3)
Alkaline : $ZnO + NaOH \rightarrow Zn(OH)_2 + 2Na_2O$ (4)

Therefore, activation of copper ions and zinc ions for the reactive dye degradation were affected by the solution pH. In comparison between both chemical catalysts, copper ions have stronger attraction forces towards reactive dye in order to destabilize the dye molecular structure compared to zinc ions.
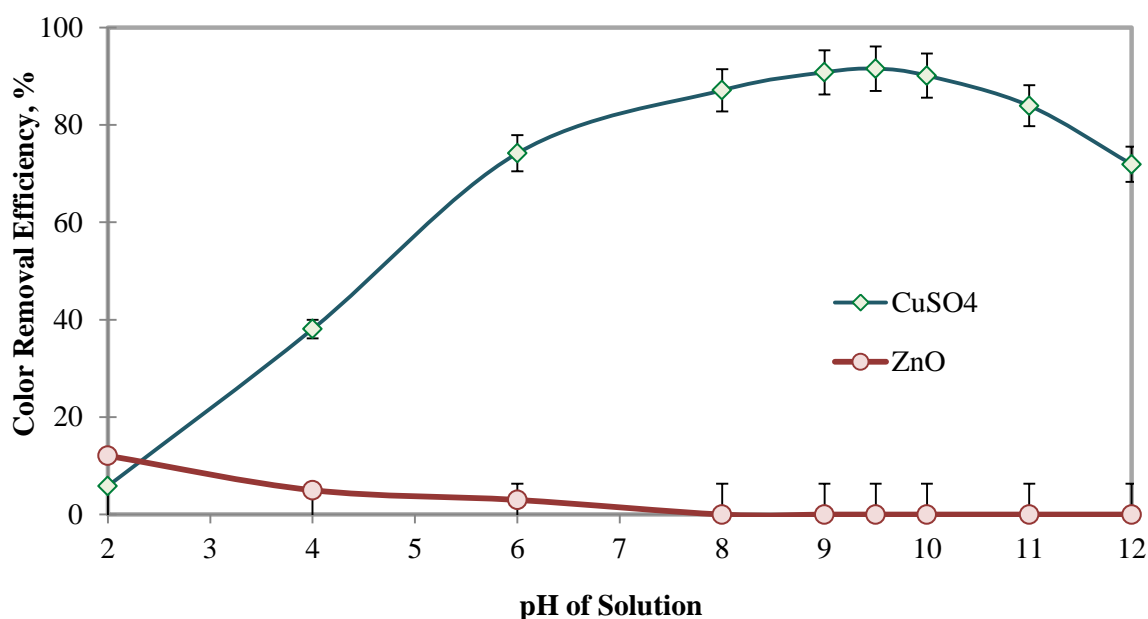
Figure 1. Color removal efficiency of RB 5 catalysed by ZnO and CuSO$_4$ with respect to pH (initial dye concentration: 100 ppm; temperature: 60 ℃; reaction time: 1 hour; catalyst mass loading: 0.5 g/L).

3.2. Extent of degradation analysis using characteristic light absorbance of dye

This research was further evaluated by using UV- Vis spectrum scanning from 200 – 800 nm to analyse the molecular structure changes for RB 5. Figure 2 presents the wavelength scan of RB 5 dye catalysed by ZnO at optimum pH 2 and CuSO$_4$ at optimum pH 9.5. Before thermolysis process, RB 5 wavelength scan presents three main chemical network strands: main band in the visible region located at 602 nm attributed to the azo linkage, UV region located at absorption bands of 325 and 270 nm were associated with naphthalene and benzene rings, respectively [14]. As the RB 5 was catalysed by ZnO at optimum pH 2, the three main chemical network strands show slight degradation. The visible region of the RB 5 shows slight decrement, indicating fragmentation of azo linkage which responsible for the color richness. Meanwhile, the slight decay of the absorbance at 325 nm indicating the destabilization of naphthalene ring whereas absorbance at 270 nm depicts the degradation of benzene ring. On the other hand, CuSO$_4$ catalyst is able to cleaved azo bond more efficiently compared to ZnO. The diazo bond in RB 5 has been broken down into single bond which attributed by the wavelength scan has been shifted to 530 nm. Moreover, the peak of naphthalene at 325 nm wavelength also reduced while the benzene peak at 270 nm increased sharply, attributed to the fragmentation of naphthalene to form benzene rings [15]. In thermalysis process, heat is transferred to energy in order to breakdown the RB 5 dye molecular structure. Sunsequently, with catalyst as the auxiliary agent, RB 5 dye degradation process was enhanced. From the result, CuSO$_4$ thermalcatalyst has greater catalytic characteristic and auxiliary agent for the molecular structure bonding fragmentation in treating RB 5 dye compared to ZnO.
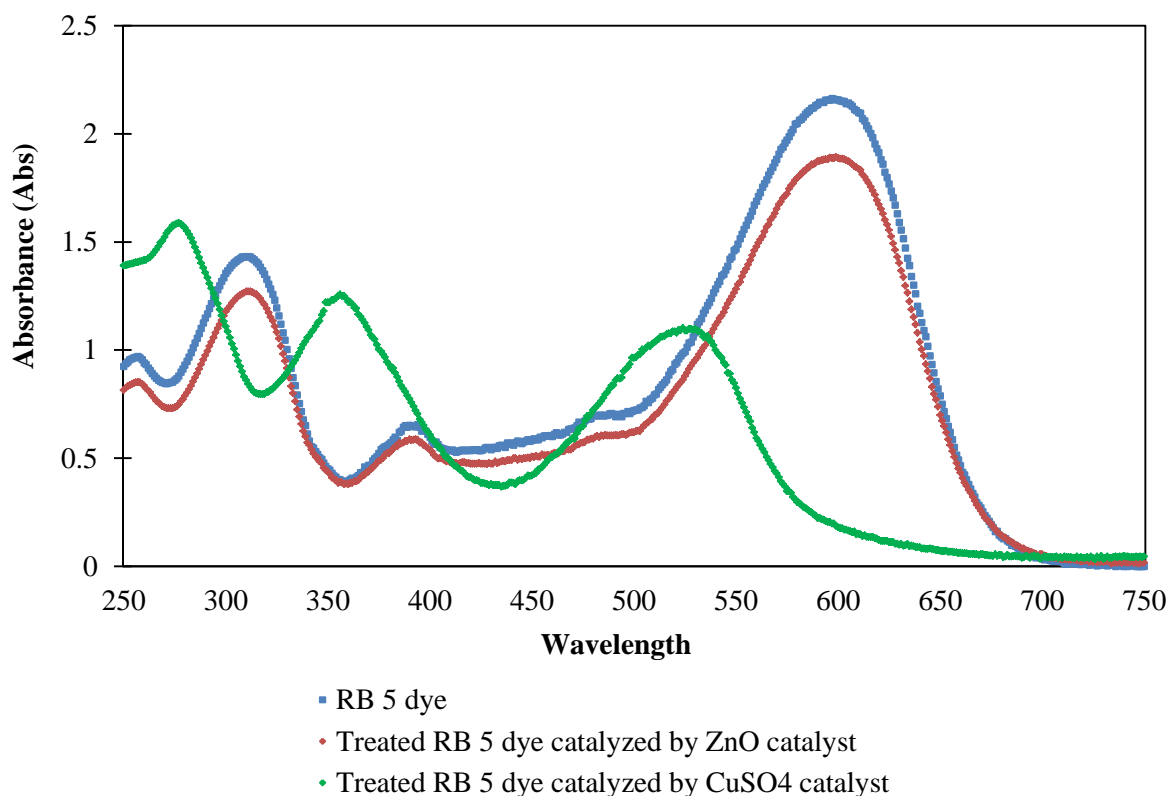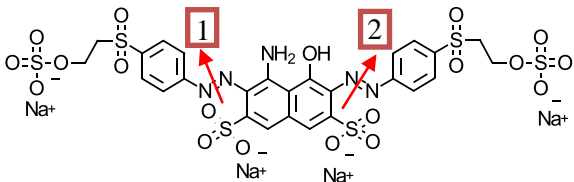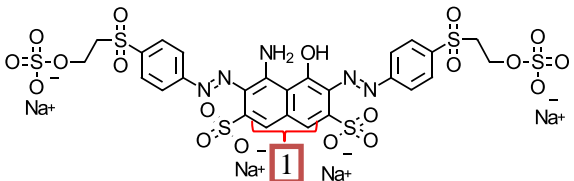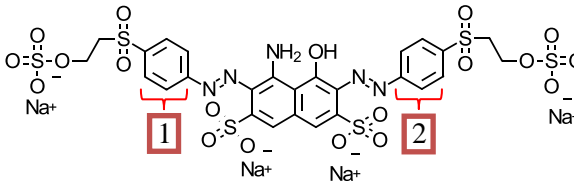
- RB 5 dye
- Treated RB 5 dye catalyzed by ZnO catalyst
- Treated RB 5 dye catalyzed by CuSO4 catalyst

Figure 2. Wavelength scan of RB 5 dye, Treated RB 5 dye catalysed by ZnO and CuSO$_4$ catalysts (initial dye concentration: 100 ppm; temperature: 60 ℃; reaction time: 1 hour; catalyst mass loading: 0.5 g/L, ZnO at optimum pH 2 and CuSO$_4$ at optimum pH 9.5).

3.3. Degradation reactions comparison of CuSO4 and ZnO as thermalcatalysts in thermolysis process
Table 1 presents the comparison between performance of CuSO$_4$ and ZnO thermalcatalysts in terms of molecular structure fragmentation of RB 5 in thermolysis process. Both CuSO$_4$ and ZnO thermalcatalysts show different levels of removal percentage analysed using the dye absorbance reduction for each of the chemical strands wavelength. The bonding of azo bond was preferentially removed in the thermolysis process. CuSO$_4$ catalyst shows higher azo bond molecular structure cleavage percentage which is around 64.42% compared to ZnO catalyst. This phenomenon is owing to the vacancies of copper ions to react with the nitrogen in azo bond [16]. On the other hand, the extent of naphthalene ring molecular structure cleavage promoted by CuSO$_4$ catalyst (73.08%) shows 15.8% higher than ZnO catalyst (4.62%) due to the difference in the removal mechanisms [17]. Whereas, a different scenario was observed for benzene ring molecular structure fragmentation. ZnO has reduced 2.66% cleavage of benzene ring, however there was increment of benzene ring when CuSO$_4$ was used as catalyst. The increment of benzene ring is due to the degradation of naphthalene ring has further degraded into benzene structure. Naphthalene ring would degrade more easily and rapidly than benzene compound since naphthalene ring is not as stable as benzene ring [18]. Therefore, CuSO$_4$ catalyst promising a better degradation capability of azo bond, naphthalene and benzene ring compared to ZnO catalyst.

Table 1. Comparison molecular structure fragmentation for $CuSO_4$ and ZnO thermalcatalysts

Molecular structure fragmentation	Percentage of removal, %	
	CuSO$_4$	**ZnO**
(i) Azo bond	Reduce 64.42%	Reduce 8.84%
(ii) Naphthalene ring	Reduce 73.08%	Reduce 4.62%
(iii) Benzene ring	Increase 11.90%	Reduce 2.66%

4. Conclusion

In this work, the degradation of diazo reactive dye (RB 5) has been studied in a thermolysis treatment using chemical catalysts ($CuSO_4$ and ZnO). On the basis of the presented investigation it can be concluded that $CuSO_4$ catalyst exhibit effective dye degradation compared ZnO catalyst since $CuSO_4$ catalyst decolorized 91.55 % of RB 5 dye at pH 9.5 whereas ZnO catalyst decolorized 7.36 % of RB 5 dye at pH 2. Additionally, this research emphasized on the degradation of the three main chemical network strands: azo bond, naphthalene and benzene rings. $CuSO_4$ catalyst could degrade 64.42 % of azo linkage, 73.08% of naphthalene ring and 11.90 % of benzene ring. On the other hand, ZnO catalyst could only degrade 8.84 % of azo bond, 4.62 % of naphthalene ring and 2.66 % of benzene ring. The presented investigation develops a new platform to utilize $CuSO_4$ catalyst in the degradation of reactive dye.

5. References

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