

Decolourisation of Reactive Orange 16 by Activated Carbon and Copper Oxide Catalysts Supported by Activated Carbon

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Abstract: *Decolourisation of Reactive Orange 16 (RO16) dye by HNO₃-modified activated carbons (ACs) and a copper oxide catalyst supported by modified AC (Cu-AC) were investigated. The percentage of colour removal for AC modified with 12 M HNO₃ acid (19%) was found to be lower than that of AC modified using 4 M and 8 M HNO₃, which are 23% and 22%, respectively. The Cu-AC, prepared by impregnating the 4 M HNO₃-modified AC with copper nitrate solution for a 5 wt% of Cu followed by calcination at 500°C in an N₂ atmosphere, shows the highest percentage of removal (63%) compared to the modified and the heat-treated modified AC. Decolourisation of RO16 by the Cu catalyst increases in the presence of H₂O₂ and UV-light. The decolourisation efficiency of the catalyst under four different conditions was observed to have the following order: Cu-AC/H₂O₂/UV > Cu-AC/H₂O₂ > Cu-ACN/UV ≈ Cu-AC.*

Keywords: modified activated carbon, copper catalyst, decolourisation, Reactive Orange 16

Abstrak: *Penyahwarnaan pewarna Reaktif Jingga 16 (RO16) oleh karbon aktif (AC) terubah suai dengan HNO₃ dan mangkin kuprum oksida terdorong di atas AC terubah suai telah dikaji. Peratus penyingkiran warna oleh AC yang diubah suai dengan 12 M asid HNO₃ (19%) didapati lebih rendah daripada AC yang diubah suai dengan 4 M dan 8 M asid HNO₃, iaitu masing-masing 23% dan 22%. Cu-Ac yang disediakan dengan mengimpregnasi 4 M HNO₃- AC terubah suai dengan larutan kuprum nitrat untuk memberi 5 wt% Cu, diikuti dengan pengkalsinan pada 500°C di bawah atmosfera N₂, menunjukkan peratus penyingkiran tertinggi (63%) dibandingkan dengan AC terubah suai dan AC terubah suai yang dikenakan rawatan haba. Penyahwarnaan RO16 oleh mangkin Cu meningkat dengan kehadiran H₂O₂ dan sinaran UV. Kecekapan penyahwarnaan oleh mangkin di bawah empat keadaan yang berbeza diperhatikan menurut aturan berikut: Cu-AC/H₂O₂/UV > Cu-AC/H₂O₂ > Cu-ACN/UV ≈ Cu-AC.*

Kata kunci: karbon aktif terubah suai, mangkin kuprum, penyahwarnaan, Reaktif Jingga 16

1. INTRODUCTION

It is well known that catalysts of metal ions in solution or powder metal oxides create an unstable state because the surface tension favours a smaller interfacial area for a given mass. Catalysts also cause a secondary pollutant problem that requires further treatment to remove the metal ion from water.¹ Therefore, attempts have been made to improve the catalysis process by replacing the homogeneous catalysts with a heterogeneous catalyst. For this purpose, supported metal catalysts can be prepared.² Activated carbon (AC) is one of the most widely used catalyst supports in recent years³⁻¹² because of its high surface area, well-defined porous structure, the presence of various surface functional groups and its inertness in many catalytic processes.⁸

Advanced oxidation processes (AOPs) are attractive alternatives to conventional treatment methods. They have been used more frequently recently due to the high oxidising power of free radicals. Production of these radicals is achieved using either single oxidants or combinations of ozone, H₂O₂ and UV radiation¹³ and a combination of H₂O₂ with ferrous ions in Fenton's reagent.¹⁴

Because copper nitrate is one of the best catalysts in catalytic oxidation of dyeing and printing wastewater, Cu is chosen to be loaded onto the porous support. This study investigates the effect of HNO₃-modified AC and its corresponding Cu-supported catalyst on the decolourisation of Reactive Orange 16 (RO16) dye. The chemical structure of RO16 dye is shown in Figure 1.

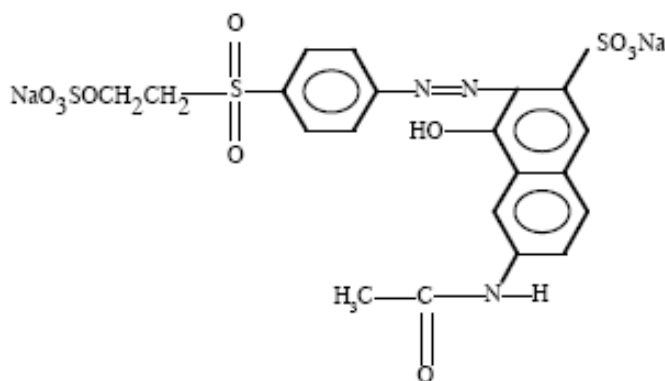


Figure 1: The chemical structure of RO16 dye.

2. EXPERIMENTAL

2.1 Activated Carbon Modification

Commercial AC (KI7060, Kekwa Indah Sdn. Bhd., Malaysia) was crushed and sieved. The carbon with a diameter between 300 and 500 μm was collected and soaked in HCl (1 M) solution for 24 h. After treatment, the samples were washed several times with hot distilled water and dried in oven at 100°C. The samples were further treated by refluxing in different concentrations of HNO₃ (1 g of AC per 10 ml of HNO₃ solution) for 4 h at 65°C. These samples were later washed thoroughly with distilled water and dried in an oven overnight at 110°C. A portion of the modified AC was calcined in an N₂ flow for 4 h at 500°C.

2.2 Catalyst Preparation

Copper oxide catalyst supported by modified AC (Cu-AC) was prepared by the impregnation method that follows: the amount of copper (II) nitrate trihydrate that will give 5 wt % of Cu was dissolved in approximately 100 ml of deionised water and later introduced into a beaker containing the modified AC. The mixture was gently heated ($\approx 60^\circ\text{C}$) with constant stirring until a thick paste was obtained. The paste was dried at 110°C for 2 h to remove the remaining water, followed by calcination in an N₂ stream for 4 h at 500°C. The preparation conditions and the modified AC and Cu catalysts are tabulated in Table 1.

Table 1: Experimental conditions for the preparation of modified AC and the corresponding Cu catalysts.

Sample	Starting material	Treatment
AC	Commercial AC	Immersed in 1M HCl, 24 h, room temperature
AC4	AC	Refluxed with 4 M HNO ₃ , 4 h, $\sim 65^\circ\text{C}$
AC8	AC	Refluxed with 8 M HNO ₃ , 4 h, $\sim 65^\circ\text{C}$
AC12	AC	Refluxed with 12 M HNO ₃ , 4 h, $\sim 65^\circ\text{C}$
AC4/500	AC4	Calcined in N ₂ flow at 500°C, 4 h
AC8/500	AC8	Calcined in N ₂ flow at 500°C, 4 h
AC12/500	AC12	Calcined in N ₂ flow at 500°C, 4 h
Cu-AC4	AC4	Impregnated with 5% Cu, calcined in N ₂ flow at 500°C, 4 h
Cu-AC8	AC8	Impregnated with 5% Cu, calcined in N ₂ flow at 500°C, 4 h
Cu-AC12	AC12	Impregnated with 5% Cu, calcined in N ₂ flow at 500°C, 4 h

2.3 Characterisation

The surface area and pore volume of the samples were analysed by N₂ adsorption at -196°C using the dynamic Brunauer-Emmett-Teller (BET) method in a Micromeritic ASAP 2000 (USA) surface area analyser. The sample was degassed at 250°C until a constant pressure at about 6×10^{-6} torr was attained. The X-ray diffraction (XRD) pattern was obtained using a Shimadzu XRD6000 (Japan) diffractometer with Ni-filtered Cu K α radiation at a scanning rate of 2° min⁻¹.

2.4 Removal of RO16 Dye

The decolourisation of RO16 (Aldrich, Singapore) was performed in a batch experiment at room temperature. 1 g of modified AC or catalysts was added to a beaker containing 1.0l of 25 mg l⁻¹ RO16 dye solution. Continuous mixing at a constant rate was provided by a magnetic stirrer for 6 h. 5 ml of aliquot was withdrawn at predetermined time intervals and filtered with a Millipore membrane (0.45 μ m) before analysis. The effect of H₂O₂ and UV light on the decolourisation of RO16 was carried out by adding a fixed amount of 1 M H₂O₂ solution and irradiating the dye solution with Blak-Ray B100 AP (Ultra-Violet Product Ltd., UK) long wave (365 nm) UV lamp. The decolourisation of RO16 was measured by a UV-Vis spectrophotometer (Lambda 20, Perkin Elmer, USA) with a λ_{max} of 492 nm.

3. RESULTS AND DISCUSSION

3.1 XRD and Surface Area and Porosity Analyses

The XRD pattern (Fig. 2) for the modified AC has a broad diffraction peak at $2\theta \approx 22^\circ$ and a sharp peak at $2\theta \approx 44^\circ$, which are assigned to the disordered graphitic 002 plane and 10 plane, respectively.¹⁵ The broad peak indicates the amorphous nature of the AC. For the Cu-AC catalyst, peaks characteristic of copper (I) oxide (Cu₂O) at $2\theta = 36.5^\circ$ and 42.4° , and copper (II) oxide (CuO) at $2\theta = 35.5^\circ$ and 38.7° were observed. The assignment of the peaks was cross-referenced with the Joint Committee on Powder Diffraction Standards (JCPDS) file for CuO (48-1548) and Cu₂O (74-1230).

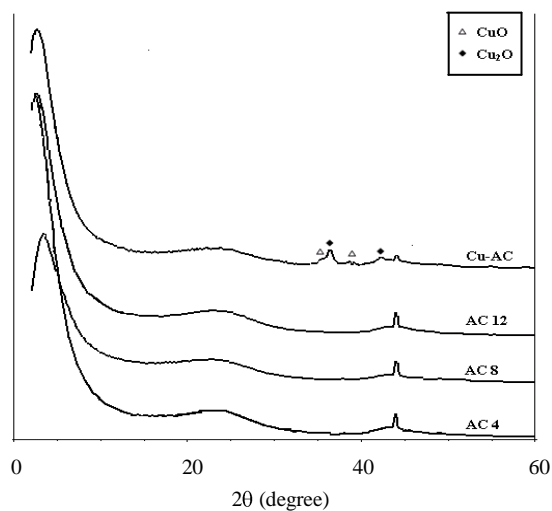


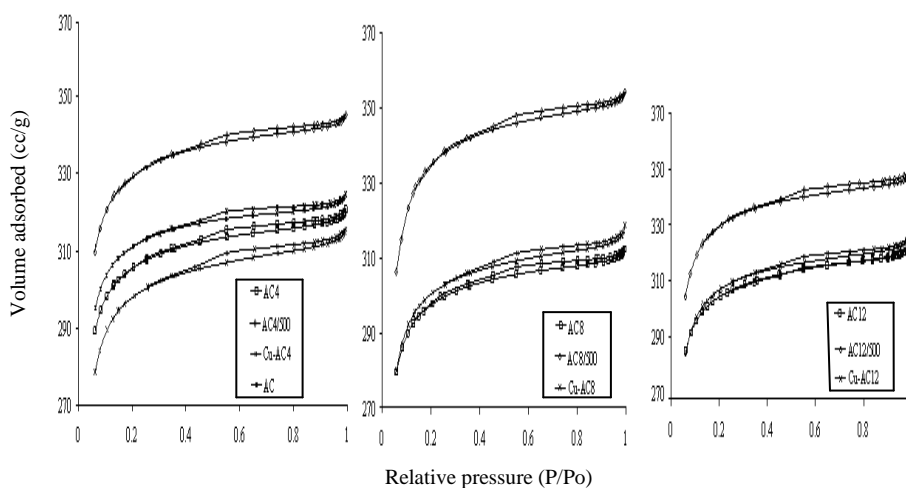
Figure 2: XRD pattern of modified ACs and Cu-AC.

Table 2 shows the surface area and porosity analysis of the modified AC and the Cu catalysts. Even though the surface area decreased as the concentration of HNO_3 increased, the difference was not significant. This indicates that HNO_3 treatment does not affect the textural properties of the AC. Instead, several researchers^{16–18} have reported that the HNO_3 treatment produced surface oxygen groups that are acidic, such as carboxyl and anhydrides, at the entrance of the micropores. Such fixation explains the observed reduction in surface area. Temperature Programmed Desorption (TPD) results^{17,18} showed that these surface oxygen groups are removed upon heat treatment. Therefore the increase in surface area that is observed for all heat-treated modified AC can be attributed to the removal of some or all of the surface oxygen groups formed during HNO_3 treatment. The reduction in surface area for Cu-AC can be explained by Cu_2O and CuO deposition onto the external surface and inner porous surface of the AC. The presence of these oxides increases the particle density, which causes the specific surface area of the catalyst to decrease.⁷

Table 2: The textural properties of modified AC and their corresponding Cu catalysts.

Sample	BET surface area (m ² /g)	Micropore area (m ² /g)	Micropore volume (cc/g)	Average pore diameter (nm)
AC	1046	850	0.40	2.8
AC4	1026	829	0.39	2.8
AC8	1023	799	0.37	2.7
AC12	1028	796	0.37	2.8
AC4/500	1108	873	0.40	2.7
AC8/500	1134	867	0.40	2.7
AC12/500	1113	825	0.39	2.8
Cu-AC4	1002	765	0.36	2.8
Cu-AC8	1015	781	0.36	2.8
Cu-AC12	1039	769	0.36	2.8

The N₂ adsorption isotherms obtained for different ACs and Cu-ACs are shown in Figure 3. All the isotherms belong to type I in the Brunauer-Deming-Deming-Teller (BDDT) classification, which is indicative of the presence of micropores of different sizes. Similar isotherms have been observed by previous studies for different activated charcoal cloth and AC samples.¹⁷ The appearance of hysteresis loops in the N₂ isotherms of samples are categorised as type H₄. The adsorption and desorption branches remain parallel over a wide range of relative pressure, which indicates the highly microporous nature of the samples.

Figure 3: Adsorption-desorption isotherms of N₂ for AC, modified AC and Cu-AC.

3.2 Removal of RO16 Dye

The removal of colour by AC is influenced by the surface area and surface chemistry of the AC. The results of the colour removal by the AC are depicted in Figure 4. The colour removal is significantly reduced when HNO₃-treated ACs are used [Fig. 4(a)]. Because the textural property of these modified ACs remains unchanged, the reduction in colour removal is attributed to the formation of surface oxygen groups during HNO₃ treatment, which increases as the concentration of HNO₃ increases. However, the colour removal was improved when heat-treated AC were employed [Fig. 4(b)] because of the removal of surface oxygen groups, especially carboxyl and anhydrides, and the increase in surface area of the ACs upon heat treatment at 500°C.

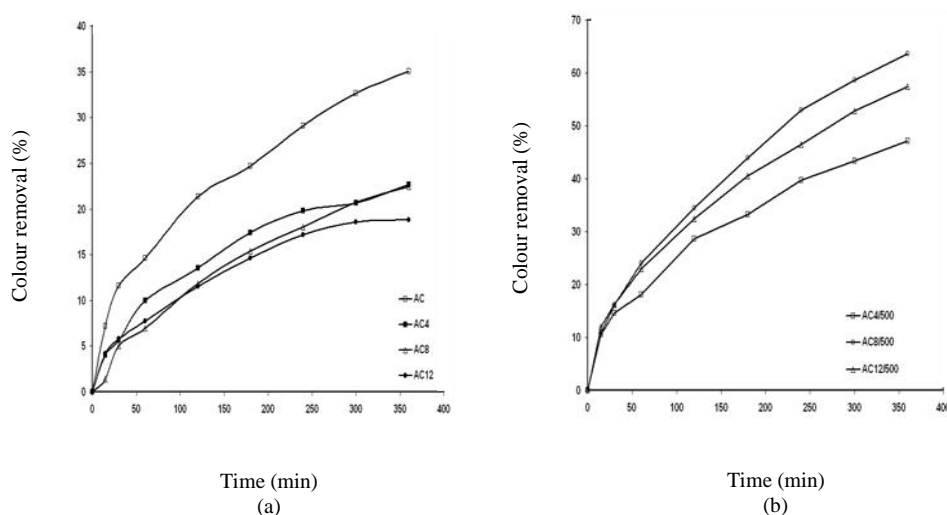


Figure 4: The percentage of colour removal of RO16 dye by (a) AC and HNO₃-modified AC and by (b) heat-treated HNO₃-modified AC.

Figure 5 shows that the colour removal percentage for the Cu-AC4 catalyst was the highest, even though it had the lowest surface area. The removal is attributed to adsorption of the dye onto the copper oxides and AC. Therefore, Cu-AC4 was chosen as the catalyst for removal of RO16 in further experiments.

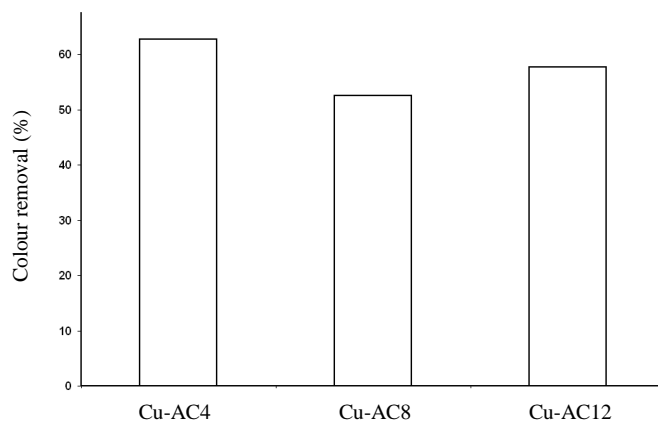


Figure 5: The colour removal of RO16 dye with Cu-AC catalysts.

3.3 Effect of H_2O_2 and UV Irradiation

Preliminary work showed that RO16 is resistant towards direct UV-photolysis and is difficult to oxidise with H_2O_2 . The combination of UV and H_2O_2 only gives 16% colour removal. The colour removal percentage by the Cu-AC4 catalyst in the presence of UV, H_2O_2 and H_2O_2 /UV are illustrated in Figure 6.

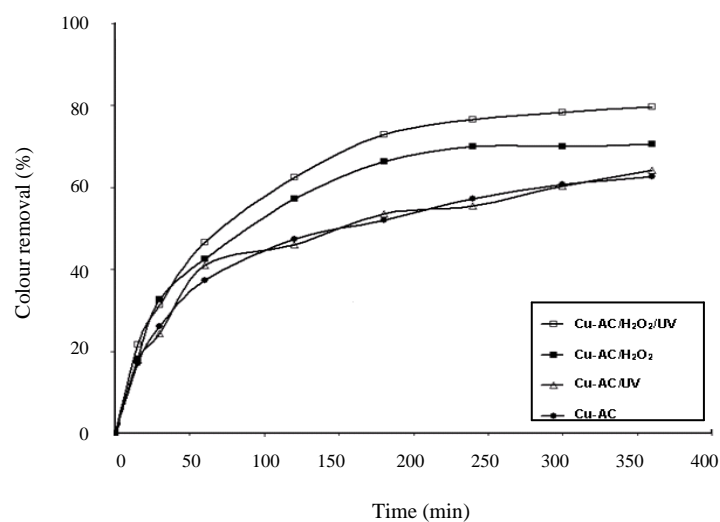


Figure 6: The colour removal of RO16 dye by Cu-AC4 catalyst in the presence of UV, H_2O_2 and H_2O_2 /UV.

The presence of H_2O_2 and $\text{H}_2\text{O}_2/\text{UV}$ enhanced the colour removal by Cu-AC4. The improvement is attributed to the formation of hydroxyl radicals, which are responsible for oxidising the dye, via copper oxide-catalysed and UV-catalysed decomposition of H_2O_2 . It should also be noted that H_2O_2 has also been used as an oxidising agent to modify the surface of AC.¹⁹ Therefore, two plausible reasons can be offered to explain the slight improvement in colour removal observed when changing from Cu-AC4 to Cu-AC4/ H_2O_2 to Cu-AC4/ $\text{H}_2\text{O}_2/\text{UV}$. First, because a portion of the H_2O_2 is used to oxidise the AC, there are fewer hydroxyl radicals available to oxidise the dye. Second, the formation of a surface oxygen group because of the reaction between the AC and H_2O_2 reduces the adsorption of dye on the AC.

It should be noted that the colour removal process occurred rapidly within the first 60 min for Cu-AC, Cu-AC/ H_2O_2 and Cu-AC/ $\text{H}_2\text{O}_2/\text{UV}$ system. However, as the contact time increases, the colour removal increases gradually. Unlike Cu-AC, the colour removal for the other systems almost reached equilibrium after 4 h. It is postulated that, during the oxidation of the dye, an intermediate that is resistant to oxidation is formed that is removed through adsorption on the AC. Because the processes of oxidation and adsorption occurred simultaneously, the AC was quickly saturated with the adsorbate, and thus, it reached its equilibrium state.

3.4 UV Spectra

The UV spectra were recorded during the colour removal process using Cu-AC, Cu-AC/UV, Cu-AC/ H_2O_2 and Cu-AC/ $\text{H}_2\text{O}_2/\text{UV}$. Similar trends were observed for Cu-AC and Cu-AC/UV and for Cu-AC/ H_2O_2 and Cu-AC/ $\text{H}_2\text{O}_2/\text{UV}$, as depicted in Figure 7. A steady decline in the intensity of the 387 nm and 492 nm peaks observed in Figure 7(a) signifies the removal of the dye through the adsorption process. The removal process is slightly different for Cu-AC/ $\text{H}_2\text{O}_2/\text{UV}$ [Fig. 7(b)]. The decline in intensity of the 387 nm peak is accompanied by a steady shift of the 492 nm peak to 540 nm. The disappearance can be attributed to oxidation of the functional group responsible for the 387 nm peak. It is therefore postulated that an intermediate formed that is responsible for the 540 nm peak, is resistant to oxidation and is removed by the adsorption process.

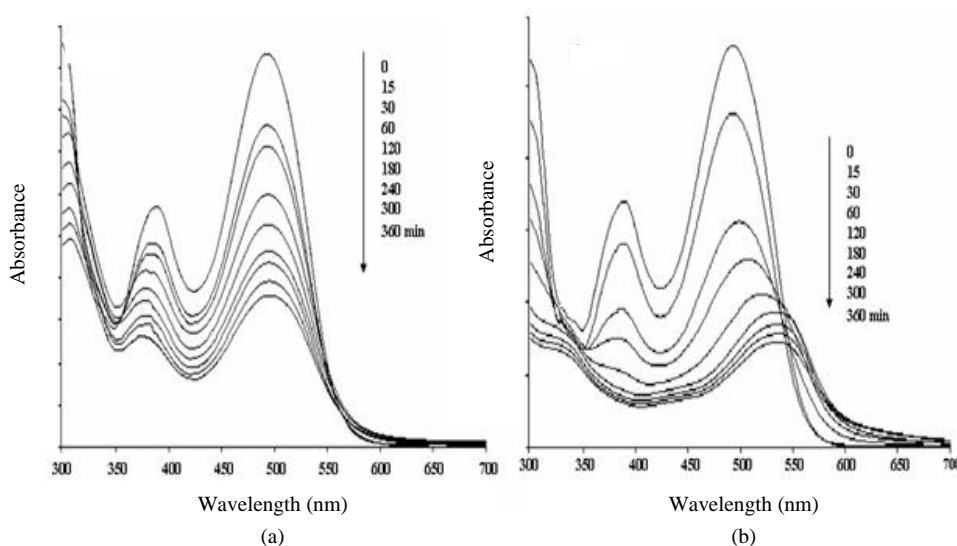


Figure 7: UV-Vis absorption spectral changes of RO16 recorded at different time intervals during (a) Cu-AC/UV and (b) Cu-AC/H₂O₂/UV process.

4. CONCLUSION

Even though the textural properties of the AC were not significantly affected by the HNO₃ modification process, the significant reduction in colour removal observed using modified AC compared to unmodified AC clearly indicates the influence of surface functional groups on the adsorption process. The colour removal is also significantly higher for Cu-AC than that for AC4/500, which is attributed to the adsorption of the dyes on the Cu oxides. The efficiency of the Cu catalyst in removing the colour of RO16 dye under different conditions is as follows: Cu-AC/H₂O₂/UV > Cu-AC/H₂O₂ > Cu-AC/UV ≈ Cu-AC. This result is due to the adsorption-oxidation process that occurs when H₂O₂/UV and H₂O₂ are used. The oxidation process is attributed to the presence of hydroxyl radical formed through copper oxide-catalysed and UV-catalysed decomposition of H₂O₂.

5. ACKNOWLEDGEMENT

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