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# Preparation of Al–Cu pillared clay catalysts for the catalytic wet oxidation of reactive dyes

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**Abstract**

Al–Cu pillared clays were prepared by direct introduction of Al–Cu pillaring solution into the dilute bentonite suspension. Al–Cu pillared clays had $d_{0\,0\,1}$ spacing of about 18 Å and had surface area of about 140 $m^2/g$ or higher. Al–Cu pillared clays showed excellent activity toward the catalytic wet peroxide oxidation (CWPO) of reactive dyes. Complete removal of reactive dyes could be achieved within 20 min at atmospheric pressure and 80 °C which are extremely milder operation condition when compared with the conventional catalytic wet oxidation process. The pillared clays were also stable against the leaching out of Cu.

*Keywords:* Catalytic wet oxidation; Al–Cu pillared clay; Reactive dye; Hydrogen peroxide; Hydroxyl radical

## 1. Introduction

Catalytic wet oxidation (CWO) has recently studied extensively to destroy organic pollutants in wastewaters [1–7]. Catalytic wet oxidation is a liquid phase oxidation of organic materials in water with oxygen (the main source of oxygen is generally air) on the surface of catalyst. Although the use of catalyst makes the reaction conditions milder than uncatalyzed wet oxidation, the catalytic wet oxidation process still requires high temperature (higher than 150 °C) and high pressure (1–5 MPa). These severe operating conditions can lead to high installation costs, and thereby practical applications of this process are limited.

The catalytic wet peroxide oxidation (CWPO) is a liquid phase catalytic oxidation with hydrogen peroxide. The catalytic wet peroxide oxidation could be a more efficient process than the catalytic wet oxidation since the oxidizing properties of hydrogen peroxide are stronger than those of molecular oxygen. Moreover, the reaction conditions when hydrogen peroxide was used as oxidant could be lowered to 80 °C and 1 atm[8,9], allowing the possibility to treat a large amount of polluted wastewater without a too large energy consumption. In our previous paper copper was proved to act as a catalyst to accelerate the decomposition of $H_2O_2$ into hydroxyl radicals ($HO^{\cdot}$)[9]. Homogeneous copper nitrate, copper chloride and copper sulfate catalysts were extremely active for the complete oxidation of organic pollutants in water into $CO_2$ and $H_2O$. However, additional separation process was necessary for the removal of copper cation before the treated water was discharged. Accordingly a new heterogeneous catalyst-containing copper cation needs to be developed for the practical application of the catalytic peroxide oxidation.

Pillared clays are thermally stable microporous solids which are promising catalysts in numerous areas [10,11]. Copper-containing pillared clay might be a promising catalyst for the successful wet peroxide oxidation of organic pollutants.

Dyehouse effluents from the textile industry impose serious environmental problems because of their color and their high chemical oxygen demand (COD)[12]. Of all the dyestuffs used the reactive dyes present major problems because they are hydrolyzed to the extent of 20% while dyeing textile substrates and therefore are discharged into the effluents in unrecoverable form. They possess high

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tinctorial power and, therefore, always exist in textile dyeing effluents.

In this study catalytic wet peroxide oxidation of reactive dyes was carried out in a batch reactor using mixed (Al–Cu) pillared clays as catalysts, and the catalytic performance of the clays was investigated.

## 2. Experimental

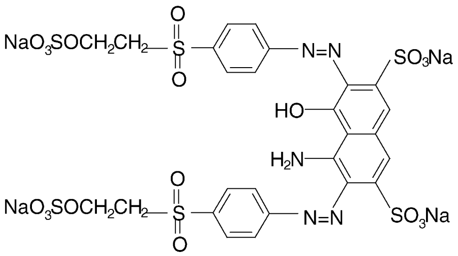
### 2.1. Materials

High purity reactive black 5 and blue 19 from Aldrich Co. were employed in this study, and the chemical structures of these dyes are shown in Fig. 1. Pure bentonite (DongYang Bentonite Co.) was used as the starting clay without any further purification procedure. Al and Cu chloride (Aldrich Co.) were used as the precursors for pillaring solution.

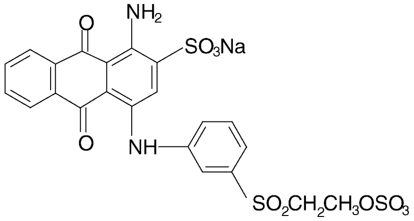
### 2.2. Catalyst preparation

Al–Cu pillared clays were prepared by direct introduction of Al–Cu pillaring solution into the dilute bentonite suspension. The pillaring solutions were prepared by dissolving 0.1 M Al and Cu chlorides in 0.2 M NaOH solution. The hydrolysis molar ratio OH/(Al + Cu) was kept to be 2. Solution volumes were adjusted to have a Cu/(Al + Cu) ratio between 0 and 20%. The pH of the solutions was about 3.8 and the solutions remained clear. The dilute bentonite suspension (1% w/w) was prepared by adding the purified bentonite powder into the corresponding distilled deionized water.

The pillaring reaction was carried out under continuous vigorous stirring at 40 °C by adding the pillaring solution drop by drop into the bentonite suspension. The prepared samples were filtered and washed with deionized water until Cl-free samples were obtained, and then dried at 120 °C for 6 h. The dried samples were finally calcined at 400 °C for 6 h.



Reactive black 5



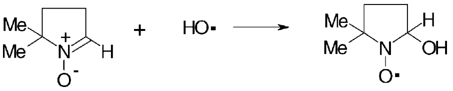
Reactive blue 19

Fig. 1. Chemical structures of reactive black 5 and reactive blue 19.

### 2.3. Reaction procedures and analysis

The oxidation of two reactive dye aqueous solution was performed in a glass reactor of 1 L capacity equipped with a condenser, stirrer and air flow controller. The reaction was conducted at atmospheric pressure and 80 °C. Air was bubbled into the solution during the reaction, and the flow rate of air was kept to be 200 mL/min.

Liquid samples were immediately filtered and analyzed for total organic carbon (TOC), $HO^{\cdot}$, color unit and residual materials in water. TOC was measured with a Shimadzu 5000 A TOC analyzer. Electron paramagnetic resonance (EPR) spin trapping of the $HO^{\cdot}$ formed during the catalytic wet oxidation was performed using a Varian E-4 spectrometer. 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO, purchased from Aldrich Co.) was used as a trapping agent because it efficiently scavenges $HO^{\cdot}$ through the following reaction to produce the DMPO/$HO^{\cdot}$ adduct, which has a characteristic EPR spectrum[9,13].



Color unit of the samples was measured by following American Dye Manufacture Institute (ADMI) tristimulus filter method [14], and $H_2O_2$ concentration was measured by a colorimetric method using a UV–vis DMS 90 Varian spectrophotometer[15]. X-ray diffraction (XRD) patterns of the Al–Cu pillared clay were recorded at a scanning rate of 18 2θ/min with a Simens D-5000 diffractometer (Cu Kα radiation). Surface area was determined by using nitrogen as the sorbate at 77 K in a static volumetric apparatus (Micromeritics ASAP2010).

## 3. Results and discussion

### 3.1. Characterization of the catalyst

X-ray diffraction patterns of the starting bentonite and Al–Cu pillared clays are shown in Fig. 2. The prepared pillared clays will be abbreviated by the symbols of Al-PILC and Al (mole% in the pillaring solution)–Cu (mole% in the pillaring solution)-PILC. Al-PILC denotes the pillared clay with alumina. Al(90)–Cu(10)-PILC is, for example, the Al–Cu pillared clay prepared by the initial pillaring solution having the 90 mole% Al and 10 mole% Cu, respectively.

The $2\theta$ angle of the (0 0 1) reflection of the pure bentonite was 7.58 which corresponded to a d-spacing of 11.77. The corresponding $2\theta$ angles of the (*hk*) two-dimensional peaks were at 19.68 and 35.38. The diffraction at $2\theta$ of 19.68 was

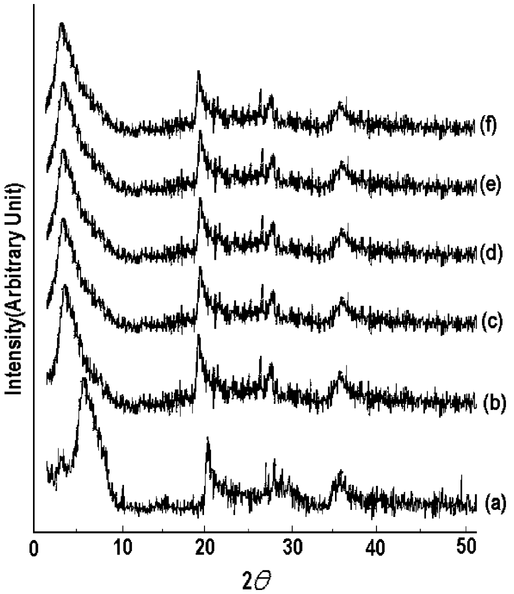


Fig. 2. XRD patterns of bentonite, a; Al-PILC, b; Al(95)–Cu(5)-PILC, c; Al(90)–Cu(10)-PILC, d; Al(85)–Cu(15)-PILC, e and Al(80)–Cu(20)-PILC, f.

the summation of *hk* indices of (0 2) and (0 1), and the diffraction of 35.38 was the summation of *hk* indices of (1 3) and (2 0). The peak at 2$\theta$ of 27.98 was a reflection of the quartz impurity[9]. Upon pillaring with Al and Cu the $d_{0\,0\,1}$ peak shifted lower 2$\theta$ values of about 4.98 corresponding to the increase in the $d_{0\,0\,1}$ spacing, while the rest of the structure was not clearly affected. The $d_{0\,0\,1}$ spacing of the pillared clays was about 18.0. In Table 1 are listed the summarized properties of the Al–Cu pillared clays. BET surface area increased significantly after intercalation.

The state of copper was also investigated by using EPR spectroscopy. When the copper was post ion-exchanged into Al-PILC sample, most of the copper existed mainly in the form of $[Cu(H_2O)_4]^{2+}$. $Cu^{II}$ was coordinated to four water molecules in the *x*–*y* plane and two surface oxygen of the silicate lattice along the *z*-axis. When the sample was fully hydrated, copper was present as $[Cu(H_2O)_6]^{2+}$ which could be easily leached out from the sample into the solution under reaction condition.

In the case of the mixed Al–Cu-PILCs, however, copper was generally grafted on the alumina pillars in the form of $[Cu^{II}(AlO)_n(H_2O)_{6-n}]^{x+}$.

Table 1
Summarized properties of Al–Cu pillared clays.

| Clay | $d_{0\,0\,1}$ (Å) | surface area ($m^2/g$) | Cu (%) |
|---|---|---|---|
| Bentonite | 11.77 | 33.2 | – |
| Al-PILC | 17.02 | 142.3 | – |
| Al(95)–Cu(5)-PILC | 18.1 | 164.5 | 0.80 |
| Al(90)–Cu(10)-PILC | 18.0 | 149.4 | 1.12 |
| Al(85)–Cu(15)-PILC | 18.0 | 146.8 | 1.71 |
| Al(80)–Cu(20)-PILC | 18.0 | 142.9 | 2.50 |

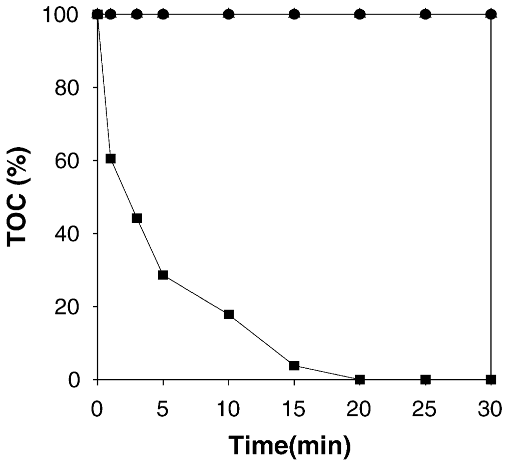


Fig. 3. Changes in TOC during the oxidation of reactive black 5 solution. (●), Uncatalyzed oxidation (without catalyst and $H_2O_2$); (▲), catalytic wet oxidation (with 10 g Al(90)–Cu(10)-PILC in the absence of $H_2O_2$); (■), catalytic wet peroxide oxidation (with 10 g Al(90)–Cu(10)-PILC and $H_2O_2$).

### 3.2. Catalytic wet peroxide oxidation of reactive dyes

To assess the extent of uncatalyzed oxidation of reactive black 5 solution, wet oxidation was performed without any catalyst and $H_2O_2$ at atmospheric pressure and 80 °C. The initial concentration of reactive black 5 solution was 1000 mg/L. As can be seen in Fig. 3, no detectable extent of the uncatalyzed oxidation of the reactive black 5 solution could be achieved. Even in the presence of 10 g Al(90)–Cu(10)-PILC alone the reaction did not proceed at all. The addition of $H_2O_2$ (20 mL, 0.5N), however, enhanced the efficiency of the oxidation remarkably. Most of reactive black 5 could successfully be oxidized within 20 min.

The addition of $H_2O_2$ to wet oxidation systems has been known to enhance the reaction rate leading to high conversion in short time [16]. The fast reaction rate of the catalytic wet oxidation with $H_2O_2$ as opposed to the uncatalyzed oxidation and the catalytic wet oxidation with air is due to the decomposition of $H_2O_2$ to give two hydroxyl radicals which react with reactive black 5 in water.

In Fig. 4 are shown the removal of TOC together with the concentration of $H_2O_2$ consumed and $HO^{\cdot}$ produced during the reaction with reactive black 5 in the presence of 10 g Al(90)–Cu(10)-PILC. The removal of TOC was shown to be strongly related to the consumption of $H_2O_2$ which will be decomposed into $HO^{\cdot}$.

A separate experiment of $H_2O_2$ decomposition in the absence of any reactive black 5 was carried out at the same reaction condition. The concentration of $H_2O_2$ was the same as that in the experiment of Fig. 4. The measured changes in the concentration of $H_2O_2$ and $HO^{\cdot}$ are plotted in Fig. 5. As seen, in accordance with the consumption of $H_2O_2$ the formation of $HO^{\cdot}$ occurs during the reaction. The rates of both the $H_2O_2$ consumption and $HO^{\cdot}$ production increased greatly by the action of Al(90)–Cu(10)-PILC which must

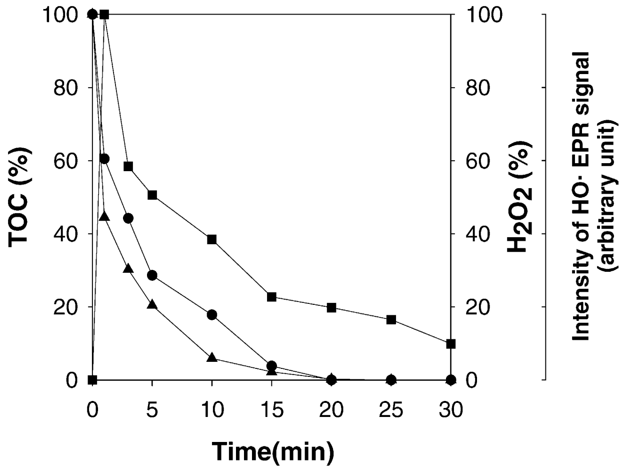


Fig. 4. Correlation between TOC removal (●), $H_2O_2$ consumption (▲) and $HO^{\cdot}$ formation (■) during the catalytic wet peroxide oxidation of reactive black 5 with 10 g Al(90)–Cu(10)-PILC.

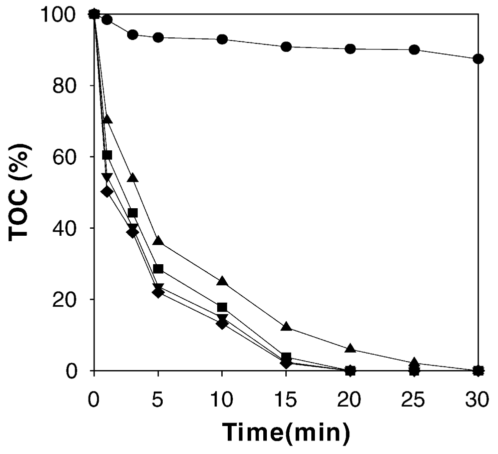


Fig. 6. Effects of Cu content in the Al–Cu pillared clays on the removal of TOC during the catalytic wet oxidation of reactive black 5 (●) Al-PILC; (▲), Al(95)–Cu(5)-PILC; (■), Al(90)–Cu(10)-PILC; (▼), Al(85)–Cu(15)-PILC; (◆), Al(80)–Cu(20)-PILC.

have played an important role on the activation of $H_2O_2$ decomposition and the subsequent $HO^{\cdot}$ formation. The subtracted amount of $HO^{\cdot}$, corresponding to the difference between $HO^{\cdot}$ formed in Fig. 5 and $HO^{\cdot}$ remained in Fig. 4 must have participated in the oxidation of reactive black 5 in water.

As discussed from the result in Fig. 5, Al(90)–Cu(10)-PILC catalyst could increase the production rate of $HO^{\cdot}$ greatly. This indicates that the use of a catalyst will further enhance the rate of oxidation of reactive black 5 solution. Fig. 6 shows a comparison between the results of wet peroxide oxidation with Al–Cu pillared clays having different amount of Cu. There was a considerable increase in the reaction rate by using Al–Cu pillared clays instead of Al-PILC. About 14% removal of TOC was achieved in 30 min with the Al-PILC, while in the presence of the Al–Cu pillared clays it took only about 20 min for the complete removal of TOC. In addition the removal efficiency of TOC increased with increasing amount of Cu in the Al–Cu PILCs.

Catalytic wet oxidation of reactive blue 19 was also conducted in the presence of 10 g Al–Cu pillared clay catalysts, 20 mL 0.5N $H_2O_2$ solution. The initial concentration of reactive blue 19 solution was 1000 mg/L. As shown in Fig. 7, reactive blue 19 could successfully be removed by using Al–Cu pillared clay as catalysts.

Fig. 8 represents the results of TOC and color unit change during catalytic wet oxidation of reactive black 5 and reactive blue 19 at five different initial $H_2O_2$ concentration in the presence of 10 g Al(90)–Cu(10)-PILC.

When the $H_2O_2$ dosage was 5 mL, the final TOC values were not significantly different from the initial values, while

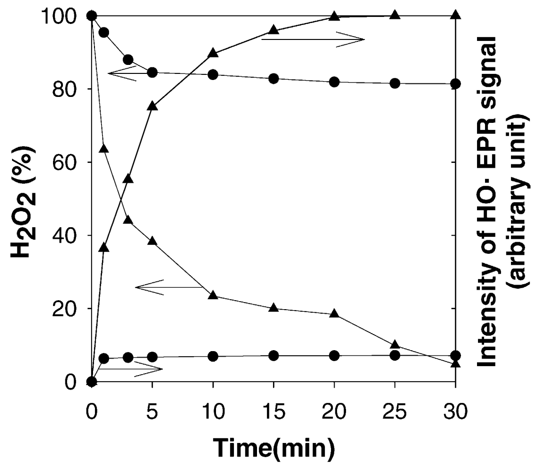


Fig. 5. Time dependence of $H_2O_2$ conversion and $HO^{\cdot}$ formation during $H_2O_2$ decomposition in the absence of the catalyst (●) and in the presence of 10 g Al(90)–Cu(10)-PILC(▲).

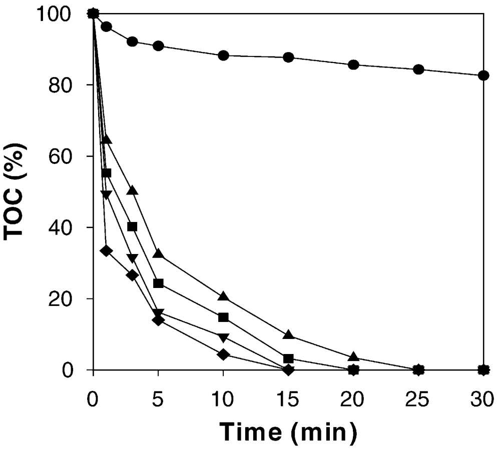


Fig. 7. Effects of Cu content in the Al–Cu pillared clays on the removal of TOC during the catalytic wet oxidation of reactive blue 19 (●), Al-PILC; (▲), Al(95)–Cu(5)-PILC; (■), Al(90)–Cu(10)-PILC; (▼), Al(85)–Cu(15)-PILC and (◆), Al(80)–Cu(20)-PILC.

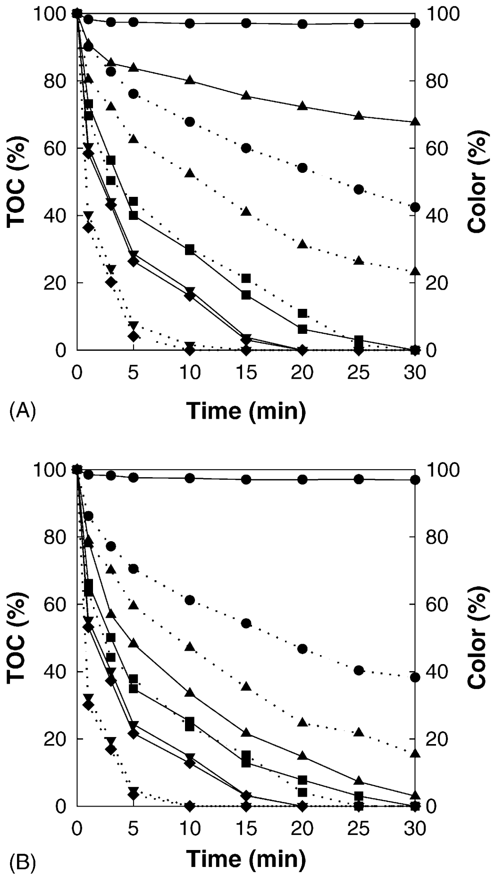


Fig. 8. Effects of concentration on the removal of TOC(–) and color(…) during the catalytic wet oxidation of reactive black 5 (A) and reactive blue 19 (B) with 5 mL (●); 10 mL (▲); 15 mL (■); 20 mL (▼); and 30 mL (◆) of 0.5N $H_2O_2$ solution.

the color units have dropped by about 60%. This means that the consumption of $H_2O_2$ does not immediately mineralize the organics in the reactive dye solution. Most of the organic carbons remain in the solution, but the newly formed organics have lower color unit per molecule. In addition both the removal of TOC and color unit was completed within 20 min when the dosage of $H_2O_2$ was more than 20 mL. These behaviors suggest that the oxidation proceeded in more than one step. The first step involves the breakdown of the large dye molecules into smaller molecules of intermediate organics. The next step will be the degradation of the smaller molecules into carbon dioxide and water.

The residual organics remaining in the solution during the reaction were analyzed and identified with a HPLC-mass spectrometer. The main organics were lower molecular weight carboxylic acids such as acetic acid, maleic acid, fumaric acid, oxalic acid and formic acid. Acetic acid and maleic acid are known to be highly refractory materials, and the oxidation of these carboxylic acids was proved to be the rate-controlling steps in the conventional catalytic wet oxidation with air [6,17,18].

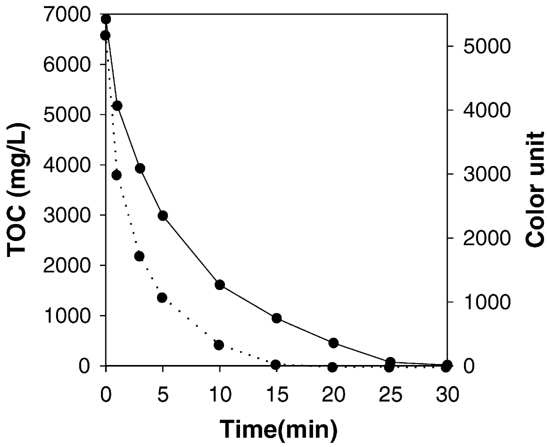


Fig. 9. Removal of TOC (–) and color (…) during the catalytic wet oxidation of a real dyehouse effluent with 10 g Al(80)–Cu(20)-PILC.

### *3.3. Catalytic wet oxidation of a real dyehouse effluent*

A real effluent, produced from the washing process of a certain dyeing industry, was employed for the catalytic wet oxidation with 10 g Al(80)–Cu(20)-PILC and 20 mL 0.5N $H_2O_2$ solution. In order for dyeing textile substrates the industry had used the aqueous solutions of reactive black 5, reactive blue 19 and reactive red 198. In addition small amount of some penetrating agents together with NaOH was contained in the effluent. The dark black reddish effluent had TOC value of 6900 mg/L and its color unit was 5200. Fig. 9 shows the time dependence of the removal of TOC and color. Most of the TOC and color unit were removed after 30 min reaction. The visual appearance of the effluent changed greatly during the reaction. The dark black reddish color began to disappear, and remained strong red color which became weaker and weaker. After 30 min reaction the weak red color was completely discolored.

### *3.4. Stability of the catalyst*

During the catalytic wet peroxide oxidation the active component Cu might be leached out from the Al–Cu pillared clays. To investigate the stability of the Al–Cu pillared clays with respect to metal leaching, the concentrations of dissolved Cu and Al in the solution were analyzed using ICP. No detectable amount of dissolved Cu and Al could be measured. Accordingly at the reaction conditions employed in this research no leaching of Cu and Al can be said to occur.

## 4. Conclusions

Al–Cu pillared clays were prepared by direct introduction of Al–Cu pillaring solution into the dilute bentonite suspension, and the prepared Al–Cu pillared clays were employed as catalysts for the wet peroxide oxidation of reactive dyes at atmospheric pressure and 80 °C.

The pillaring reaction for the preparation of Al–Cu pillared clays was performed at 40 °C with OH/(Al + Cu) molar ratio of 2 and at Cu/(Al + Cu) ratio of 0, 5, 10 and 20%, respectively.

Upon intercalation the $d_{0\,0\,1}$ spacing increased from 11.77 to 18.0. In addition the surface area of the pillared samples also increased from 33.2 $m^2/g$ of the pure bentonite upto 164.5 $m^2/g$.

Al–Cu pillared clays were proved to act as excellent catalysts for the wet peroxide oxidation of reactive dyes. The initial 1000 mg/L reactive dyes could be completely removed in just 20 min with 10 g Al(90)–Cu(10)-PILC at atmospheric pressure and 80 °C. The catalysts were also extremely stable against the leaching out of active Cu component into the aqueous solution.

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