A novel heterogeneous acid-activated clay supported copper catalyst for the photobleaching and degradation of textile organic pollutant using photo-Fenton-like reaction

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Copper supported on acid-activated bentonite clay was found to be an effective catalyst for the photo degradation of Acid Black 1 at pH 3.0–8.0 without significant metal leaching.

The conventional Fenton reaction, which was first observed in 1894, has been reviewed by various researchers and its performance has been validated for different catalytic applications over the years.[1] Later, many investigations demonstrated that, when accompanied by UV illumination, the Fenton reaction showed significant enhancement in its catalytic degradation of organic pollutants in water.[2a,2b] The organic pollutants can be effectively oxidised or mineralised to CO_2 and H_2O. Such a reaction system, with the presence of both UV irradiation and hydrogen peroxide, is known as the photo-Fenton reaction if ferrous ion is used as the catalyst or as the photo-Fenton-like reaction if Cu or Cr ion is used. These reactions have been widely applied in heterogeneous catalysis for environmental applications. However, the leaching of metal ions from the heterogeneous catalyst has always been a problem until recently, when an iron-containing clay was developed as a stable catalyst.[2b,2c] Many researchers have reported that the photo-Fenton reaction has outstanding performance at pH 3.0,[2b,2d] whereas its performance is reduced dramatically at pH values higher than 3.0.[2e] This weakness prevents the photo-Fenton heterogeneous catalyst from being applied in wastewater treatment since organic wastewater often has a pH higher than the value of 3.0. To adjust the pH of large volume of wastewater to the value of 3.0 by adding acid is too costly and inapplicable. The photo-Fenton-like reaction using Cu ions as the catalytic element appears to be a possible solution because it shows acceptable activity over the pH range of 3.0–8.0.[3] However, the heterogeneous Cu supported catalyst has severe leaching problems at low pH due to the ion activity favouring the acidic environment. The severe leaching of Cu ions would result in an increase of heavy metal that leads to serious water contamination. To overcome such a limitation, it is necessary to modify the catalyst support so that Cu can be anchored or bonded onto the support surface firmly.

Bentonite clay is one kind of smectite clay that has a very similar structure to montmorillonite. Its aluminosilicate layers are negatively charged due to isomorphous substitution. When found in nature, often the negative charges of these layers are compensated by the cations between the layers. In aqueous state, the negatively charged aluminosilicate layers attract water molecules to the interlayer for charge balance. This charge balance phenomenon allows swelling and cation exchange to take place. Such properties can therefore be used to intercalate a desired cation into the clay lattice.[4a] The clay-based metal composites prepared by this ion-exchange method have shown their activities in various pioneering works in the field of catalysis. For example, a mixed Al and Fe pillared laponite clay catalyst showed its performance in wet peroxide oxidation[4b] and syngas conversion;[4c] zirconium intercalated clay as a support for a nickel catalyst worked effectively for methane reforming with CO_2.[4d]

The objective of this work is to produce a heterogeneous catalyst with minimum leaching during the reaction, as well as to search for a method that keeps the activity of the catalyst over a wide range of pH. Bentonite clay, denoted by "-Ben", supplied by Sigma Chemical Co., America, was selected as the catalyst support throughout our studies. Cu and Fe were introduced into the bentonite clay by chemical vapour deposition (CVD) and sol-gel techniques, respectively. To overcome the leaching problem of Cu ions from the heterogeneous catalyst, a pre-treatment was employed to treat the bentonite clay with H_2SO_4 prior to the deposition of Cu by CVD. Such a procedure has an activation effect on the bentonite clay and is referred to as "acid activation".[5]

The untreated or natural bentonite clay contains various cations that may take up the active sites in the clay structure, resulting in reduction of the catalytic power of the catalyst. It is believed that acid activation is able to provide enough hydrogen ions to displace the cations that compensated the negative charge in the layers. It can be seen from the chemical composition results (Table 1) that the untreated bentonite clay contains more cations, in terms of wt%, compared to that of the bentonite clay treated with acid. The bentonite clay, therefore, is said to be "purified" by the acid treatment. The activated bentonite clay is denoted by "-ABen" and the Cu-activated bentonite clay is denoted by "Cu-ABen" in this work. The prepared Cu-ABen catalyst has a BET surface area of

Table 1 Bulk chemical compositions measured by XRF

Element	Pure bentonite (wt%)	Acid-activated bentonite (wt%)	Cu-ABen (wt%)
O	53.74	58.43	53.89
Na	1.13	0.37	0.41
Mg	1.41	1.10	1.25
Al	9.75	8.14	8.29
Si	30.35	23.01	29.48
S	0.17	6.44	1.84
K	0.19	0.00	0.02
Ca	0.78	0.30	0.36
Ti	0.10	0.08	0.09
Fe	2.38	2.13	1.91
Cu	0.00	0.00	2.46

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145 m^2 g^{-1} and a Cu wt% of 2.46. The surface atomic composition of the Cu-ABen catalyst was measured by XPS and the results (atomic %) are C1s: 3.69, O1s: 62.58, Mg1s: 1.23, Al2p: 10.02, Si2p: 20.75, Fe2p: 0.91, Cu2p: 0.82. The Cu supported by the untreated bentonite clay is denoted by "Cu-Ben" for comparison.

Acid activation was performed by suspending the bentonite clay in the presence of H_2SO_4. Cu was then deposited onto the surface of the acid-activated bentonite clay by CVD.† A textile organic dye, Acid Black 1 (AB1), $C_{22}H_{14}N_6Na_2O_9S_2$, was used as the model pollutant for this work. Eqn. (1) describes the overall chemical reaction for the oxidation of AB1 by H_2O_2. The catalyst was evaluated under the reaction conditions of 0.1 mM Acid Black 1 and 6.4 mM H_2O_2 concentration based on the reaction stoichiometry, as well as illumination by a 1 × 8 W UVC lamp and at an ambient temperature of 30 °C. The Fe-bentonite clay catalyst, Fe-Ben, used in this work was produced by the so-called sol-gel technique. The maximum leaching of Fe from the Fe-Ben catalyst was recorded to be 1.6 ppm. The catalyst concentration was 0.5 g L^{-1} for Cu-ABen or Cu-Ben, and 1.0 g L^{-1} for Fe-Ben unless specified. The pH was adjusted to 3.0, 5.3 (unadjusted natural pH of AB1 solution) and 8.0. The duration of each experiment was set to be 120 min, timed as soon as the UVC lamp was switched on. A UV-vis spectrophotometer (Shimadzu UV-1206) and TOC analyser (Shimadzu TOC-5000) were used to monitor the photobleaching and degradation of AB1, respectively. The metal concentration in the solution was measured with an inductively coupled plasma atomic emission spectrometer (Perkin Elmer 3000XL).

$$\begin{aligned} &C_{22}H_{14}N_6Na_2O_9S_2 + 64H_2O_2 \rightarrow \\ &22CO_2 + 67H_2O + 6HNO_3 + 2NaHSO_4 \end{aligned} \quad (1)$$

Fig. 1 shows the photobleaching of AB1 as a function of time. It is important to note that the photobleaching only refers to the removal of "visual" organic dye, and that the original dye could be transformed to multiple intermediates prior to complete degradation of organics. The absorbance of AB1 was measured at wavelength 610 nm and it is the only compound absorbing at this wavelength. It can be seen that both Cu- and Fe-bentonite catalysts were able to achieve more than 95% colour removal of AB1 in 120 min. The catalytic performance of both catalysts was particularly sensitive to pH. Fe-Ben showed a remarkable performance at pH 3.0 (trace 1) that almost 98% discoloration was obtained in 30 min. A significant drop in activity, however, was observed at pH 5.3 and pH 8.0 (traces 2 and 3) as reported by previous researchers.[2d,2e] It is observed that the discoloration of AB1 with 0.5 g L^{-1} Fe-Ben loading at pH 3.0 (trace 4) appeared slower than that with 1 g L^{-1} Fe-Ben (trace 1). Fig. 1 also illustrates the photobleaching using Cu-ABen at pH 3.0, pH 5.3 and pH 8.0 (traces 5–7), whereas the importance of acid activation of bentonite is highlighted by the comparison between Cu-ABen and Cu-Ben at pH 3 (trace 10). Comparing Cu-ABen and Cu-Ben (traces 5 and 10) at 15 min, it is found that acid activation improves the discoloration of AB1 by nearly 25%. Moreover, unlike Fe-Ben, Cu-ABen holds the activity at pH 5.3 and pH 8.0 (traces 6 and 7) so that more than 80% AB1 discoloration is achieved at 30 min. In addition, Cu-ABen performs equally well as Fe-Ben, in terms of discoloration, at pH 3.0. It is, therefore, evident that Cu-ABen shows better competency in terms of pH compared to Fe-Ben, even though the dosage of Cu-ABen was only half of Fe-Ben (0.5 *vs.* 1.0 g L^{-1}).

The total organic carbon (TOC) in the reaction solution was measured as an indicator for the organic mineralization at different time intervals. Fig. 2 shows the TOC removal at pH 3.0, pH 5.3 and pH 8.0 with Cu-Ben, Cu-ABen and Fe-Ben. Similar to the results in photobleaching, Fe-Ben gave TOC removal of 89% at pH 3.0 (trace 1) and its performance declined quickly to below 20% at pH 5.3 and pH 8.0 (traces 2 and 3). These results further prove that Fe-Ben is undesirable at pH values higher than 3.0. Fe-Ben also demonstrated a slower rate of TOC removal when

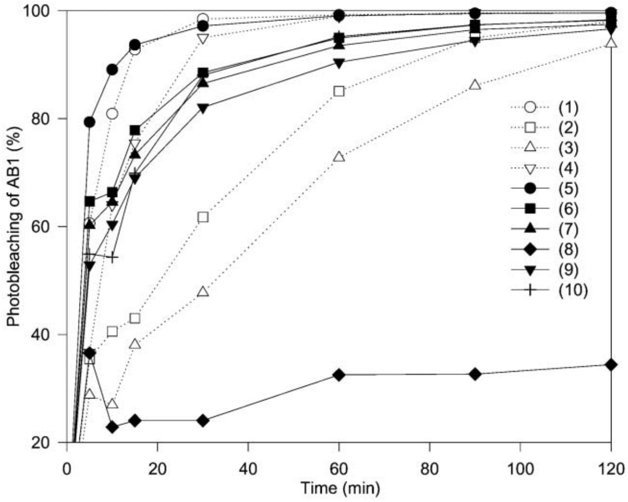

Fig. 1 Photobleaching of AB1. [Traces: (1) Fe-Ben pH 3.0, (2) Fe-Ben pH 5.3, (3) Fe-Ben pH 8.0, (4) Fe-Ben pH 3.0 (0.5 g L^{-1}), (5) Cu-ABen pH 3.0, (6) Cu-ABen pH 5.3, (7) Cu-ABen pH 8.0, (8) Cu-ABen pH 5.3 without H_2O_2/UVC, (9) Cu-ABen pH 5.3 without UVC (10) Cu-Ben pH 3.0].

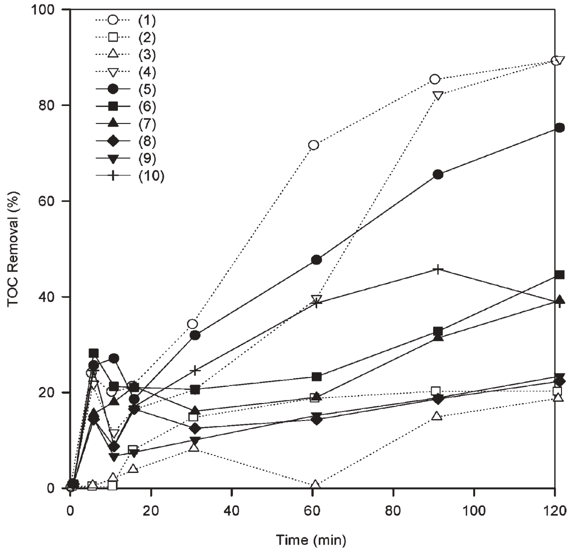

Fig. 2 TOC removal of AB1. [Traces: (1) Fe-Ben pH 3.0, (2) Fe-Ben pH 5.3, (3) Fe-Ben pH 8.0, (4) Fe-Ben pH 3.0 (0.5 g L^{-1}), (5) Cu-ABen pH 3.0, (6) Cu-ABen pH 5.3, (7) Cu-ABen pH 8.0, (8) Cu-ABen pH 5.3 without H_2O_2/UVC, (9) Cu-ABen pH 5.3 without UVC (10) Cu-Ben pH 3.0].

$0.5\ g\ L^{-1}$ loading was used (trace 4). It is observed that Cu-ABen exhibits reasonable performance at pH 3.0 (trace 5) and almost 75% of TOC removal was recorded in 120 min duration, whereas less than 45% TOC removal was reached at pH 5.3 and pH 8 (traces 6 and 7). Nevertheless, it is important to recall that Fe-Ben was only able to achieve less than 20% TOC removal at pH 5.3 and pH 8.0. Furthermore, the rate of TOC removal with Cu-ABen seems to be increased notably after 60 min. This is most likely because the organic intermediates that were formed in this particular time interval could be degraded easily compared to those existing before 60 min. From both the photobleaching and TOC removal at pH 3.0, pH 5.3 and pH 8.0, Cu-ABen was shown to be satisfactory in a wider pH range compared to Fe-Ben. The significance of acid activation to the catalytic activity was shown, once again, by the comparison between the performance of Cu-ABen and Cu-Ben at pH 3.0 (traces 5 and 10). A massive improvement was recorded that TOC removal at 120 min was increased by almost 40% if acid activation was carried out for the original bentonite clay prior to the deposition of Cu. This provides strong evidence that acid activation is indeed an essential preparation step for the Cu-bentonite clay catalyst. Additionally, the adsorption property of Cu-ABen was demonstrated by an adsorption test in the absence of H_2O_2 and UVC (trace 8). Approximately 21% TOC removal was recorded after 120 min. This result suggests that Cu-ABen is a dependable adsorbent for the acid dye, in particular, AB1, but the major degradation is from the catalytic oxidation. The importance of illumination is explained by comparing the TOC removal at pH 5.3 in the presence and absence of UVC (traces 6 and 9, respectively). The TOC removal in the presence of UVC (trace 6) was recorded as 44% whereas in the absence of UVC, only 22% TOC removal was achieved. Clearly, the illumination of UVC improves the oxidation drastically in the reaction. This is an expected result as the UVC and Cu^+/Cu^{2+} system has a recycling effect that conserves the presence of Cu^+ and Cu^{2+} in the reaction, leading to fast generation of hydroxyl radicals from H_2O_2 for oxidation needs. At this point, irradiation with UVC is confirmed as a significant factor for this catalytic organic degradation method.

Leaching of Cu at pH 3.0 is of particular interest in this work. Fig. 3 shows the Cu ion concentration in the reaction solution over 120 min. It is apparent that Cu-Ben had almost 12 ppm Cu leaching after 120 min (trace 6), while Cu-ABen had only 3.3 ppm leaching recorded (trace 1). This significant improvement could be due to the enhancement of chemical bonding between Cu and the acid-activated surface of the bentonite clay. Such strong bonding restricted the Cu available to be leached out from the surface under the acidic conditions. The leaching of Cu in 120 min at pH 5.3 and pH 8.0 (traces 2 and 3) was 3.1 and 1.7, respectively.

From this work, it is believed that acid activation of clay plays a crucial role in the heterogeneous catalyst synthesis that significantly minimises the Cu ion leaching problem. The developed Cu-ABen is able to show reasonable photobleaching and TOC removal activity for a model textile dye, Acid Black 1, at pH 3.0, pH 5.3 (natural pH) and pH 8.0 with acceptable Cu leaching. In comparison with Fe-Ben, this acid-activated Cu/clay catalyst displays more advantages in terms of performance at a wider pH range.

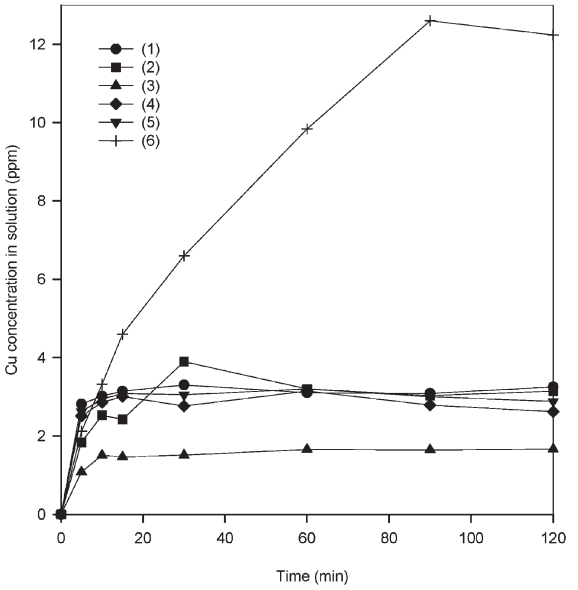

Fig. 3 Leaching of Cu. [Traces: (1) Cu-ABen pH 3.0, (2) Cu-ABen pH 5.3, (3) Cu-ABen pH 8.0, (4) Cu-ABen pH 5.3 without H_2O_2/UVC, (5) Cu-ABen pH 5.3 without UVC, (6) Cu-Ben pH 3.0].

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Notes and references

† 10 g of bentonite clay was suspended in 40% (w/w) H_2SO_4 for 4 h under vigorous stirring. The activated bentonite clay was then separated by centrifugation and dried in an oven for 24 h. Chemical vapour deposition (CVD) of Cu was carried out at 250 °C for 1 h with copper(II) acetylacetonate as the Cu source.[6] The Cu-activated bentonite composite was then calcined at 350 °C for 24 h followed by a hydrogen reduction process at 275 °C for 6 h.

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