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Preparation and Characterisation A Catalytic System Cu-Clay for Catalytic Oxidation of Methyl Orange with H_2O_2

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ABSTRACT: In this work, the decolorization of Methyl Orange was conducted using catalysts prepared by impregnation of copper on natural clay in the presence of H_2O_2. The catalysts Cu-clay, prepared from the concentrated metal precursor of (impregnation ratio, $W(Cu(NO_3)_2)/W(clay)$ = 1,5%–7,5%) were characterized by several methods such as X-ray diffraction (XRD), electronic scan microscopy (SEM), x-ray fluorescence (FX), and Brunauer–Emmett–Teller (BET).

Important factors affecting catalyst activity and methyl orange removal efficiencies were studied: the effects of temperature, oxidant concentration, and catalyst dosage. The results showed, a very significant activation of hydrogen peroxide by the catalyst, the Methyl Orange depletion percentage reaching 94 % after 2 h, and very stability of the catalyst. It was also observed that the best catalyst, at a reaction temperature of 25°C. 2,5ml of H_2O_2 and 4.0 g/L of 5% Cu-clay, 94% decolorization was achieved within 120 min treatment. Although the Cu show high activity, their stability and reusability still need improvement.

KEYWORDS: catalytic wet peroxide oxidation, Azo dye, decolorization, impregnation, clay.

I. INTRODUCTION

In recent years, one of the environmental concerns more studied is the efficient and affordable recovery of water resources contaminated with toxic organic compounds, from this kind of compounds, phenols and azo dyes have received much attention [1].

Azo dyes are the most frequently used among all dyes, comes mainly from the textile industry, providing toxic and highly coloured water streams wherein the of solar radiation is significantly restricted, decreasing seriously the photosynthetic activity of biological agents in the aquatic environments affected [2]. The degradation of these dyes is necessary before they were discharged into the environment. Hence, the treatment of these azo dyes wastewaters is becoming a matter of great concern.

The traditional physical, biological and chemical process could not remove pollutants effectively, sometimes just transferred them from one phase to another, rather than destroying them [3].

process Wet air oxidation WAO is very useful for treating a variety of refractory organic pollutants in wastewater, but the high pressure (0.5–20 MPa) and high temperature (175–320°C) required for its operation limit its practical applications [4] therefore, catalytic wet peroxide oxidation (CWPO) is proposed to relax the oxidation conditions [5] represents an interesting alternative to treat this kind of effluents, using solid catalysts makes the process more attractive by achieving high conversion at considerably lower temperature and pressure. In catalytic wet peroxide oxidation CWPO processes, the presence of transition metals oxides such as Fe_2O_3, CuO, MnO_2, CoO, ZnO has been proven to be useful for promotion of different reactions, Many references report iron and copper as very active catalytic agents in the oxidation of refractory organic compounds with peroxide, based on the Fenton mechanism [6, 7], iron and copper mainly used to decompose catalytically hydrogen peroxide into $OH^{\bullet}$ radical dot radicals at mild conditions [4].

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A disadvantage of using iron precursors is that the reaction should be carried out at pH values around 3. In turn, copper has a similar role as iron in catalysing hydrogen peroxide to produce hydroxyl radical, with the advantage that this reaction still retains a high efficiency at a higher pH range [8-10]. However, Catalytic wet peroxide oxidation of reactive dyes could be successfully carried out with Cu-based catalysts. Several heterogeneous catalysts with Fe or Cu impregnated clay have been prepared for CWPO [11, 12].

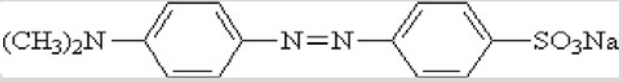
In this paper, the catalytic activity of Cu-clay catalyst with an azo dye, methyl orange, as a model pollutant in CWPO was investigated. Clay was impregnated with copper at various concentrations and the resultant Cu-clay catalysts were used in the CWPO of methyl orange in aqueous solution. Catalyst activity and characteristics, particularly pore properties, were assessed in detail. The efficiency of the incorporation of copper into the structure of a clay and stability of the catalysts was also assessed by XRD.

II. MATERIALS AND METHODS

II-1 CHEMICALS AND REAGENTS

Hydrogen peroxide (30%, w/w), Copper (II) nitrate $Cu(NO_3)_2$, and MB were purchased from Sigma–Aldrich . All the reagents used for this experiment were analytical grade and were used without further purification. Deionized water was used for all the experiments. An azo dye, methyl orange, was chosen as the target compound, and its chemical structure is as shown in Table 1.

The clay used as the carrier of catalyst had the chemical composition 37,86% SiO_2. 10,43% Al_2O_3. 4,65% Fe_2O_3. 0.06% MnO. 2,52% MgO. 18,72% CaO. 0.26% Na_2O. 2,34% K_2O.

Table 1	Structure and characteristics of Methyl Orange
Dye	Methyl Orange
Molecular formula	$C_{14}H_{14}N_3NaO_3S$
Chemical structure	
Azo type	Mono-azo
Other names	Sodium 4-[(4-dimethylamino)phenylazo] benzenesulfonate
Molecular weight (g/mol)	327.33

II-2 CATALYST SUPPORT PREPARATION

The catalyst support is clay, originating in the area of Oulja, Morocco. Prior to its use, the gray colored clay was grinded to powder using laboratory mortar and washed several times with ultrapure water (MILLIPORE, direct-Q, UV3 with Pump) water to remove impurities. The samples were dried in an oven at 100 °C for overnight, to obtain clay purify [13].

II-3 PREPARATION METHOD OF CATALYST

The Catalyst (Cu-clay) was prepared supporting the metal by the impregnation method [14]. In this process, Specific amount of $Cu(No_3)_2.3H_2O$ (1.5–10 wt.% of copper ions in the catalyst) was dissolved in a beaker containing 50 mL of distilled water. Then, clay was added to this aqueous solution, stirred constantly of the beaker was kept at 120 rpm and 100°C until all water was evaporated. After impregnation, the sample was dried at 105 °C for overnight, followed by calcination at 500°C for 4 h. The obtained catalysts are denoted as xCu-clay, where x is the molar percentage of Cu in the mixture, based on [Cu/(Cu + clay) × 100%].

II-4 CHARACTERIZATION OF CATALYST

The phase compositions of the as-prepared sample were characterized by X-ray diffraction (XRD) the Panalytical company using Cu Kα (λ = 1,54060 nm) radiation, functioning to 40 kV and 30 mA. The data were collected with 2θ = 10°-80°. Electronic Scan Microscopy (MEB), characterizations were performed on a MEB-EDX,(Quanta 200 FEI equipped with probe EDAX for microanalysis of surfaces). The clay characterized by XRF, uses a sequential spectrometer AXIOS PANALYTICAL with a channel of measurement bases on only one goniometry covering the complete range of measurement of B to U.

II-5 EXPERIMENTAL PROCEDURE AND ANALYTICAL METHODS

For the MO degradation study on Cu/clay, a stock solution of 4.6×10^{-5} mol/L was prepared. In each degradation study, 10 mL of the stock solution was mixed with 2.5 mL H_2O_2 (30%) and 4g/l Cu-clay. The catalyst was introduced methyl orange solution with magnetic-stirring to maintain a uniform suspension. After allowing 15 min for the adsorption/desorption of MO to reach equilibrium, H_2O_2 was added into the reactor and time logged. Throughout the reaction, Solutions of dye were prepared by using ultrapure water (MILLIPORE, direct-Q, UV3 With Pump) and the reactant solution was adjusted to constant pH with dilute aqueous HCl 0.01M or NaOH 0.01M solutions. the taking away were carried out by filtered using a syringe filter of diameter 0,45µm (Minisart, sartorium stedim biotech).The degradation progress was monitored by spectrometric measurements using a spectrophotometer (Jasco V530) with its adsorption at 465nm for samples that had pH> 3 and at 500nm for samples that had pH≤3 [15].The effects of various experimental parameters such as the temperature, catalyst dosage, and H_2O_2 amount were investigated. The average degradation in terms of the percentage of MO in solution was calculated using the following formula:

$$\text{Decolorization efficiency } (\%) = \left[\frac{A_o - A_t}{A_o}\right] \times 100\% \qquad (1)$$

A_o is the initial absorbance of dyes solution and A_t is the absorbance of the dyes at time t [16, 17].

III. RESULTS AND DISCUSSION

III-1 CHARACTERIZATION OF THE PREPARED CATALYST

- **ANALYSIS OF XRD RESULTS**

XRD was used to analyze the CuO form loaded on catalyst. This component is indicative of the presence of copper in the impregnated catalyst. The results are gathered in Figure 1.

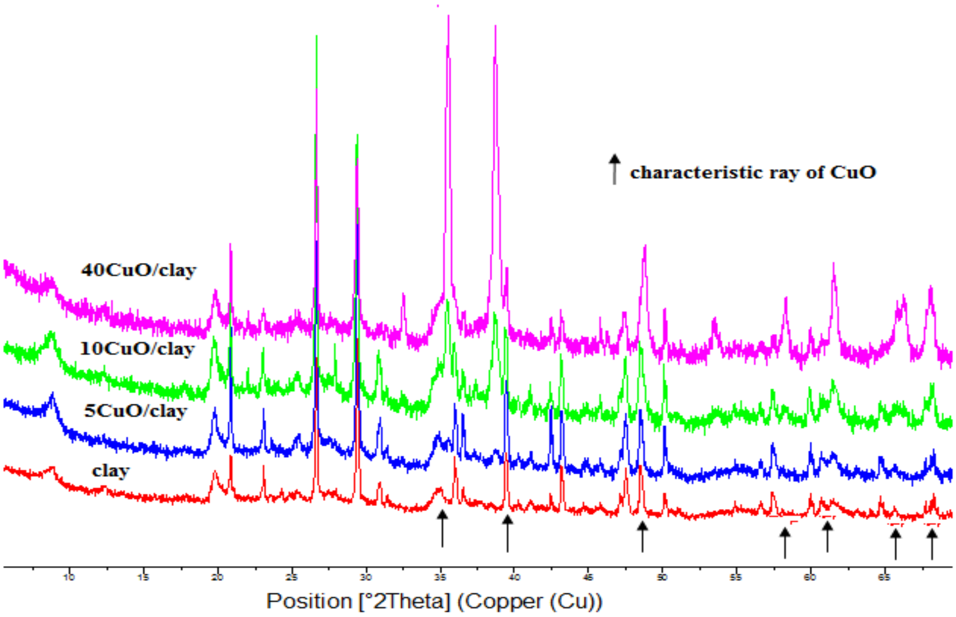


Fig. 1. Powder XRD patterns of CuO-clay samples at varying the Cu molar ratios in comparison to that of clay

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the Fig. 1, shows the characteristic peaks of CuO (Tenorite, syn, monoclinic, JCPDS#41-254) around 35.53°, 38.74°, 48.48°,56.61°,61.52°,66.29° and 68.09°, and this intensity increased with increased copper content. This indicates that higher loading of copper in catalyst preparation led to form the higher levels of copper oxide on the activated carbon in the catalyst.

- **Analysis of BET results**

The specific surface areas of the catalysts were determined using the Brunauer–Emmett–Teller (BET). The results shown in the Figure 2 showed that the surface area decreased with increasing the copper content. This maybe because copper hydroxyl nitrate deposited on the surface and filled in the pores of the clay [18, 19].

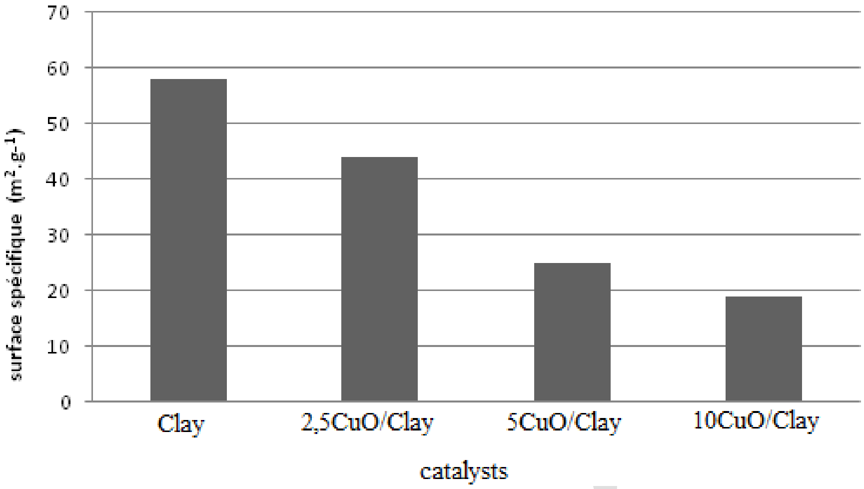

Fig. 2. The BET surface area of clay and catalysts prepared by the different Cu molar ratios.

- **SEM image**

The SEM image is used to probe the change in morphological features of clay and clay impregnated by different molar ratios of copper hydroxyl nitrate. It can be seen from Figure 3 reveal that surface morphology of the clay is different from the one impregnated.

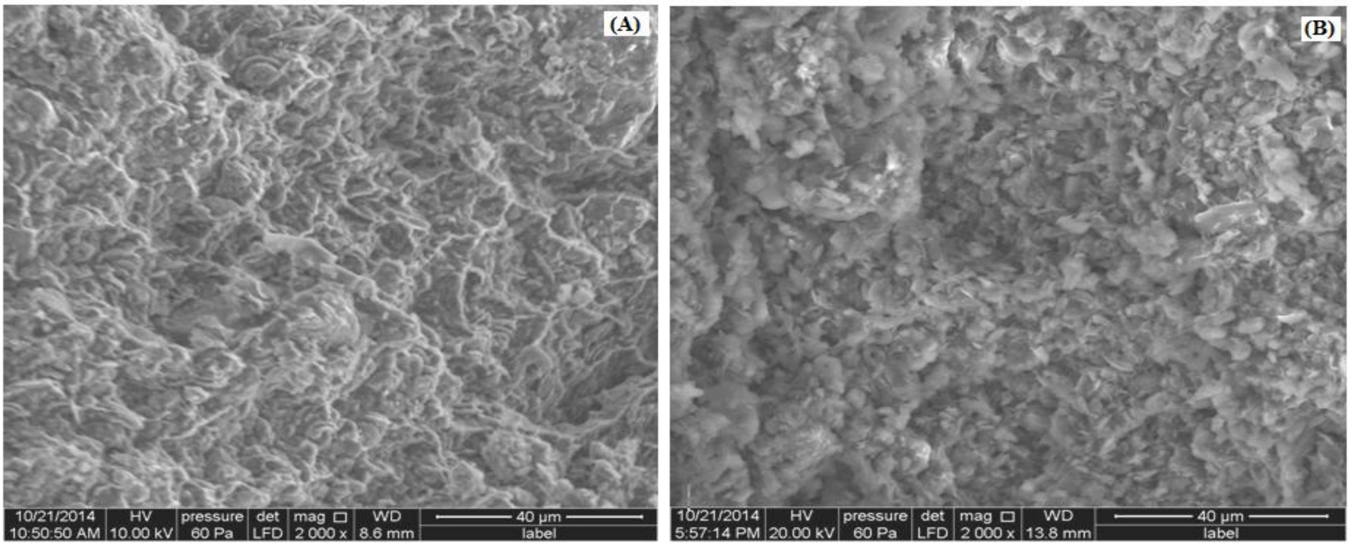

Fig. 3. SEM images of (A) clay (B) 5% Cu/clay.

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After impregnation process by copper hydroxyl nitrate, the clay has become more porous and fluffy. This porous and fluffy appearance probably was due to the change in the surface charge of the particle as a result of impregnation process and reduction in certain amorphous phase originally associated with the clay.

The EDX microanalyses were employed to perform elemental analyses in the clay and catalysts. The EDX results suggest that the content of Cu was found to increase in the catalysts with increased Cu molar ratios. The results are gathered in Figure 4.

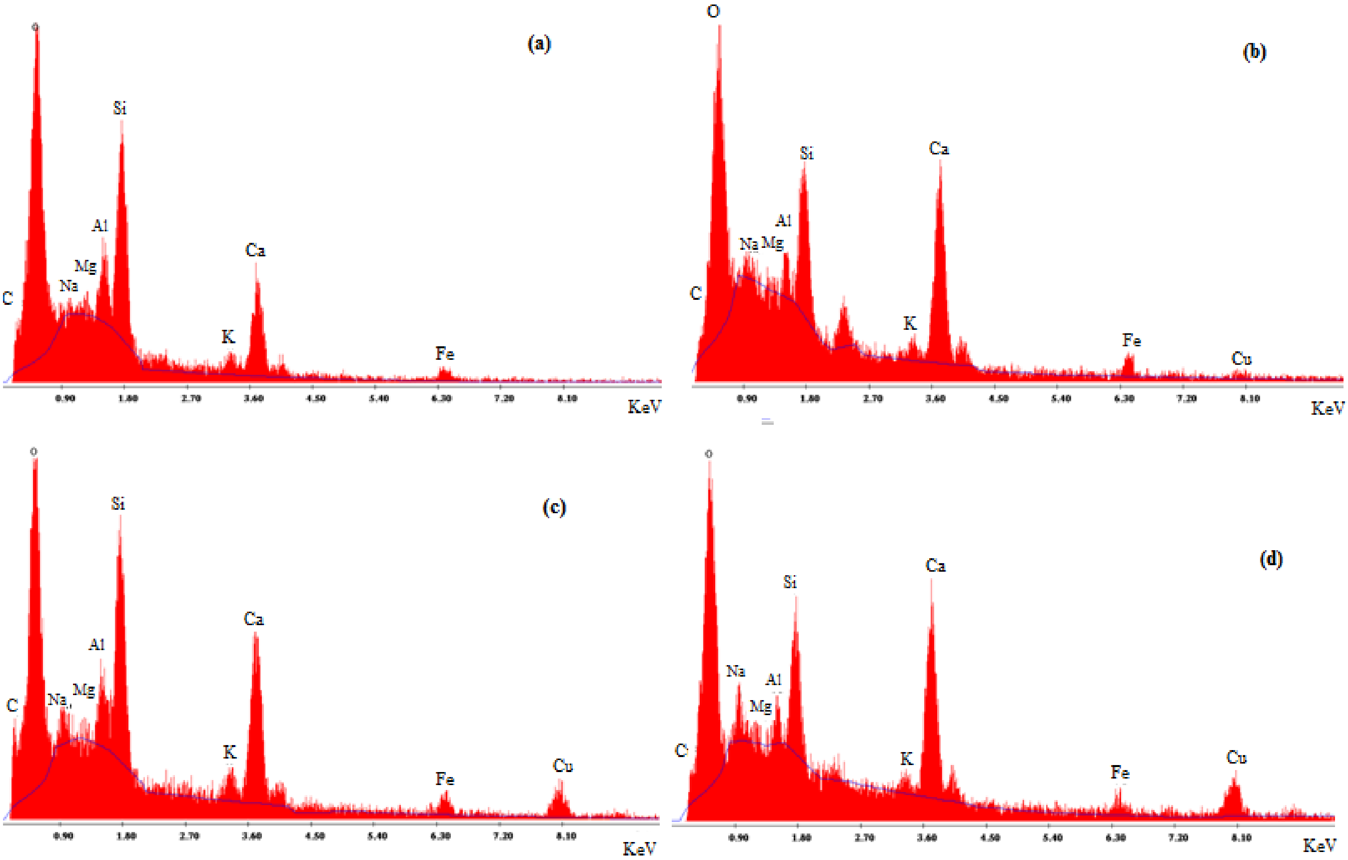

Fig. 4. EDX analysis of the clay and Cu/clay at various Cu molar ratios (a) Clay, (b) 1,5Cu-clay, (c) 5C-clay and (d) 7,5Cu-clay respectively.

III-2 EFFECT OF VARIOUS EXPERIMENT PARAMETERS ON DEGRADATION OF METHYL ORANGE.

- **Effect of catalyst loading.**

A number of reports have demonstrated that catalyst dosage has a large influence on the reaction rate [20, 21]. To investigate the effect of Cu-Clay addition on dye degradation, six different catalyst loadings (0, 10, 20, 30, 40, and 50 mg) were tested. Figure 5 displays the decomposition rate of MO with different catalyst dosages. There was a critical dosage (40 mg) of the catalyst, at which the decolorization efficiency was the best. A maximum dye removal of 97%was observed at 40 mg followed by 96% at 50 mg and 95%, 84% at 30, 10 mg respectively in 3 h duration. The % dye removal without catalyst was very low with only 44% dye removal in 3 h. By comparing the results for the dye removal without catalyst and 40 mg catalyst, the removal for 40 mg is approximately two times to that of without catalyst. The rate of removal is also more for higher concentrations of catalyst and increases with it.

The effect of catalyst dosage on the decolorization rate can be explained as follows. When a very small amount of catalyst was used, the catalyst was well dispersed in the reaction medium, and thus all active surface sites were available. Accordingly, the rate increased with catalyst dosage. Once the catalyst dosage reached a certain amount (40 mg in this study), the adsorption of MO onto the catalyst surface reached an optimum state. The decrease of catalytic activity at higher catalyst dosages was because all dye molecules were adsorbed on the catalyst and the addition of a larger amount of CuO would have no effect on the degradation rate, while there was increased opacity of the reaction suspension [22].

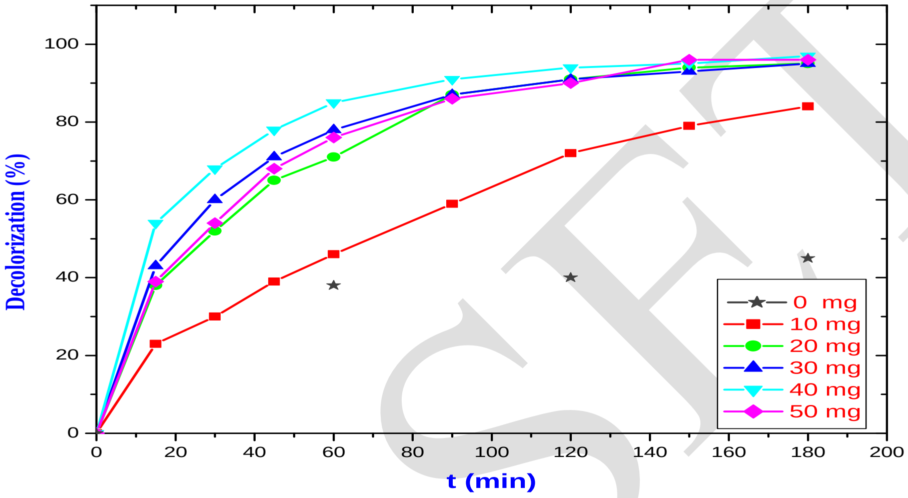

Fig. 5. Effect of catalyst dosage on the decolorization of MO.(reaction conditions: 2.5 mL 30% H_2O_2, 10 ml MO 15 mg/L, catalyst 5Cu-clay , T = 20 °C, pH= 7.0).

- **Influence of copper impregnation on dye oxidation.**

The performance in decolorization of aqueous methyl orange (MO) solution, per the Cu-clay were examined over a period of time as shown in Figure. 6 which displays the effect of copper loading on clay on the decolorization of Methyl Orange. The results indicated that the decolorization of Methyl Orange is remarkably dependent on the copper ions concentration at fixed initial concentration of hydrogen peroxide and Methyl Orange. It would be observed that with an increase in the amounts of copper ions concentration from 1.5 to 5 wt.%, the decolorization of Methyl orange slowly increased until it reached the maximum value. This can be attributed to the increased production of more $^{\bullet}OH$ radicals in the system. Also, 98% decolorization was achieved for 5 wt.%, within 180 min. However, with further increase in the amount of copper ions beyond the 5 wt.%, the decolorization efficiency of Methyle Orange reduced. This may be explained by the fact that higher concentration of copper ions could lead to the scavenging of $^{\bullet}OH$ radicals by copper ions and induce the decrease in decolorization of Methyl Orange [23].

$$Cu^{2+} + H_2O_2 \rightarrow Cu^{+} + HO_2^{\bullet} + OH^{-} \qquad [24]$$

$$Cu^{+} + H_2O_2 \rightarrow Cu^{2+} + HO^{\bullet} + HO^{-} \qquad [25]$$

$$Dye + HO^{\bullet} \rightarrow [Dye\ (HO^{\bullet})] \rightarrow oxidation\ products \qquad [25]$$

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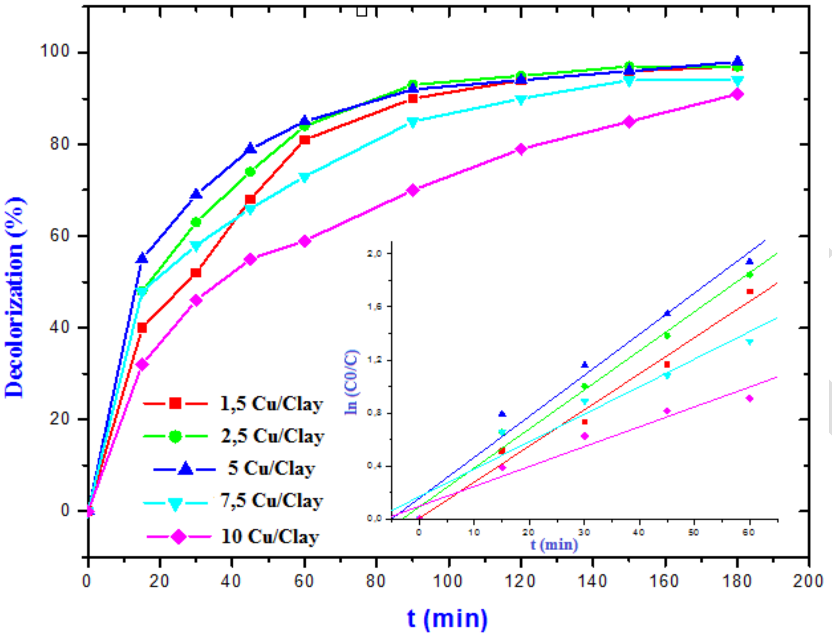

Fig. 6. Effect of copper loading on clay on the decolorization of MO. (reaction conditions: 2.5 mL 30% H_2O_2, 10 ml MO 15 mg/L, catalyst loading = 40 mg, T = 20 °C, pH= 7.0). Inset: kinetic of methyl orange oxidation catalyzed by Cu-Clay as a function of Cu dosage

Fig. shows a plot of ln(C_0/C) vs. time for the catalytic degradation of MO in the presence of the Cu-clay. The first-order kinetic model derived from the Langmuir–Hinshelwood kinetic equation was used to quantify the catalytic efficiency of the cu-clay by calculating the respective first-order rate constants (k) according to the following equation:

$$\ln\left(\frac{C_0}{C}\right) = kt \qquad (2)$$

Where C_0 and C are the initial and reaction concentrations of MO at time t [17]. The linear regression plots fitted well, from which the slopes of each plot were calculated and used to obtain the first-order rate constants (k). The k for MO degradation were found to be k1,5Cu-clay=1,6344 S^{-1}, k2,5Cu-clay= 1,7658 S^{-1}, K5Cu-clay=1,8564 S^{-1} , K7,5Cu-clay=1,2438 S^{-1} and k10Cu-clay=0,8988 S^{-1}. The k represents the catalytic activity of the catalyst. The higher the k value, the faster the degradation of MO, hence, better catalytic activity of the Cu-Clay.

- **Effect of initial pH**

The solution pH significantly influences the degradation of organic compounds. The influence of pH on the dye oxidation was studied; the effects of pH were examined by adjusting the initial pH of dye solution in the range 3–7. The results indicate that the catalytic activity of Cu-Clay increases with the increase of initial pH (Figure.7). Similar conclusions have been reported when using copper as active species to degrade organic contaminant, through either heterogeneous [26, 27]. Or homogeneous processes [28-30].

In this study, the degradation efficiency of MO after 60 min was 72, 78 and 84% at pH values of 3.0, 5.0, and 7.0, respectively. The optimal pH range for the degradation is 5–7. A near-neutral pH condition is preferable because operation under near-neutral conditions can easily apply to most wastewater.

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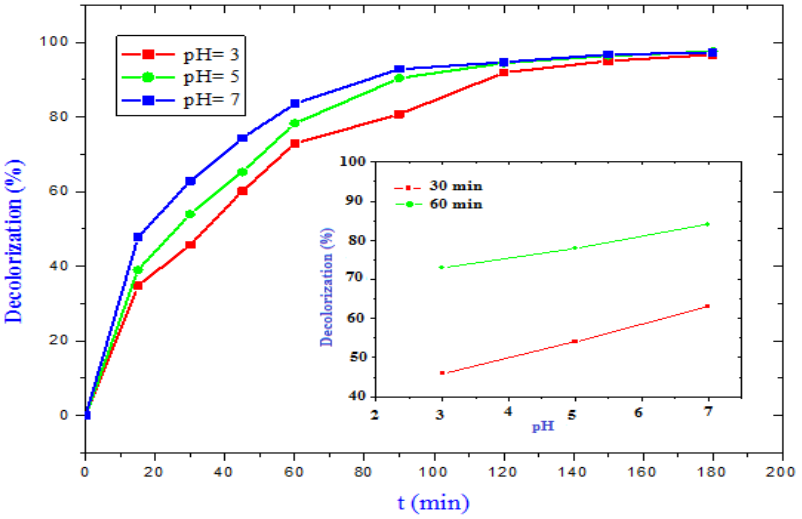

Fig. 7. Effect of pH on the decolorization of MO. (reaction conditions: 2.5 mL 30% H_2O_2, 10 ml MO 15 mg/L, catalyst loading = 40 mg, T = 20 °C, pH= 7.0). Inset: relationship of pH and dye degradation at 30 and 60 min, respectively.

- **Effect of peroxide concentration on dye**

The influence of H_2O_2 concentration on dye removal (Methyl Orange) is shown in Figure 8. A maximum removal of 79% was obtained at H_2O_2 concentration of 3 ml per 10 ml of solution at 2h, followed by 77% at 3,5 ml and 71% at 2,5 ml. The dye removal at H_2O_2 concentrations of 2 ml and 1,5 ml (and at 2 h) were 64% and 55%, respectively. More than 0.5 mL H_2O_2 results in a decrease in initial reaction rate. This means that there is an optimal concentration of H_2O_2 to degrade organic contaminants.

The addition of H_2O_2 is known to increase the rate of dye degradation by allowing an enhancement in the formation of hydroxyl radical. Consequently, the degradation rate is expected to be enhanced. But at high dosage, H_2O_2 is a powerful $HO^•$ scavenger [23].

Addition of excess of H_2O_2 results in a decrease in reaction rate. This phenomenon can be explained by the scavenging effect of excess H_2O_2, which decreases the number of hydroxyl radicals in the solution [24].

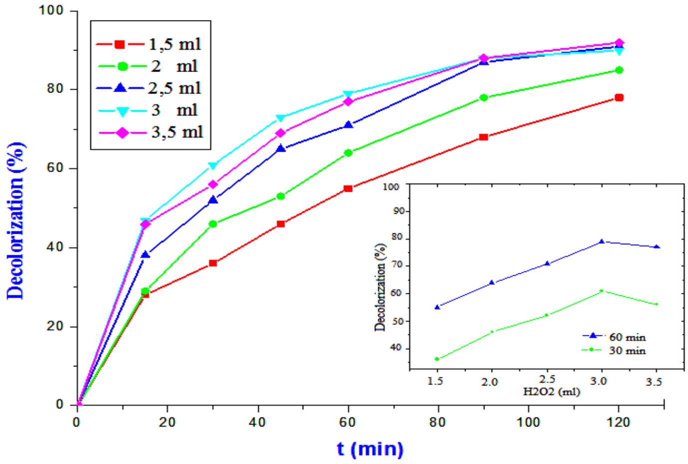

Fig. 8. Effect of H2O2 dosage on the catalytic degradation of Methyl Orange (pH= 7.0, 10 ml MO 15 mg/L, catalyst loading 5Cu-Clay = 40 mg, T = 20 °C). Inset: relationship of H_2O_2 dosage and dye degradation at 30 and 60 min, respectively.

- **Effect of temperature**

The influence of temperature on the Methyl Orange removal using catalyst was studied by varying the temperature from 20 to 60°C. The results are given in Figure 9.

As can be seen from Figure 9, rising temperature significantly enhanced the catalytic activity of MO degradation. At 60°C the degradation efficiency of MO reached about 86% and 98% after 15 and 60 min, respectively. The dye removal is much higher at higher temperatures (60°C). This is because higher temperature increased the reaction rate between hydrogen peroxide and the catalyst, thus increasing the rate of generation of oxidizing species such as $^{\bullet}$OH radical or high-valence copper species [25, 31] . The degradation efficiency after 15 min was 49% , 55% and 70% at 20, 30 and 50 ◦C, respectively. Complete decolorization is achieved in 1 h at 60°C as against 3 h at 20°C. This shows that higher temperature may be employed in cases where a faster rate of decolorization is required.

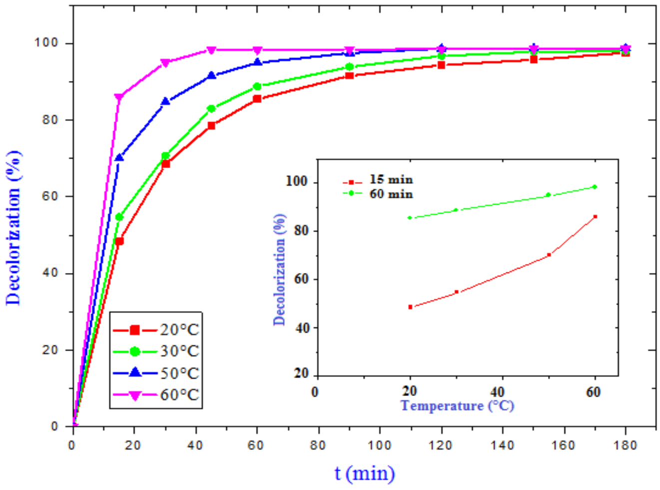

Fig. 9. Effect of temperature on the catalytic degradation of Methyl Orange (pH= 7.0, 2.5 mL 30% H_2O_2, 10 ml MO 15 mg/L, catalyst loading 5Cu/Clay = 40 mg). Inset: relationship of temperature and dye degradation at 15 and 60 min, respectively.

- **The Reusability of catalyst**

The results of stability tests conducted to assess the catalytic activity of Cu-clay catalyst through four consecutive experiments with the same catalyst load under the same reaction conditions show that the decomposition efficiency of MO decreased with recycle number. At the end of each cycle, the catalyst was washed with distilled water three times followed by drying in an oven. As can be seen from Figure 9A the decolorization efficiency of 150 mg/L of methyl orange in 1 h decreases from 84% for the first cycle to 71% for the third cycle. Nevertheless, when the catalyst was further reused without treatment in the 4th Cycle, it was found that the MO removal efficiency dropped from 84% to about 42% as reported in Figure. 10(A).

Therefore, the used catalyst after the 3rd run requires suitable regeneration prior to further use. There is several possible regeneration methods include refluxing method, calcination under a suitable atmosphere, rinsing by appropriate solvent or some combinations of processes [6, 32] and [33]. The deactivated 5Cu-clay catalyst was regenerated rinsing in by 5% HCl solution for 5 min followed by drying at 110°C for 2 h, to remove the unreacted MO, the catalytic activity of fresh catalyst was compared with the catalytic activity of regenerated catalyst under the same condition. It can be seen from Figure.10(B) that rinsing in hydrochloric acid is an effective regeneration method, giving the removal efficiency of 83%. The catalytic activity of the regenerated catalyst is very close to its initial activity.

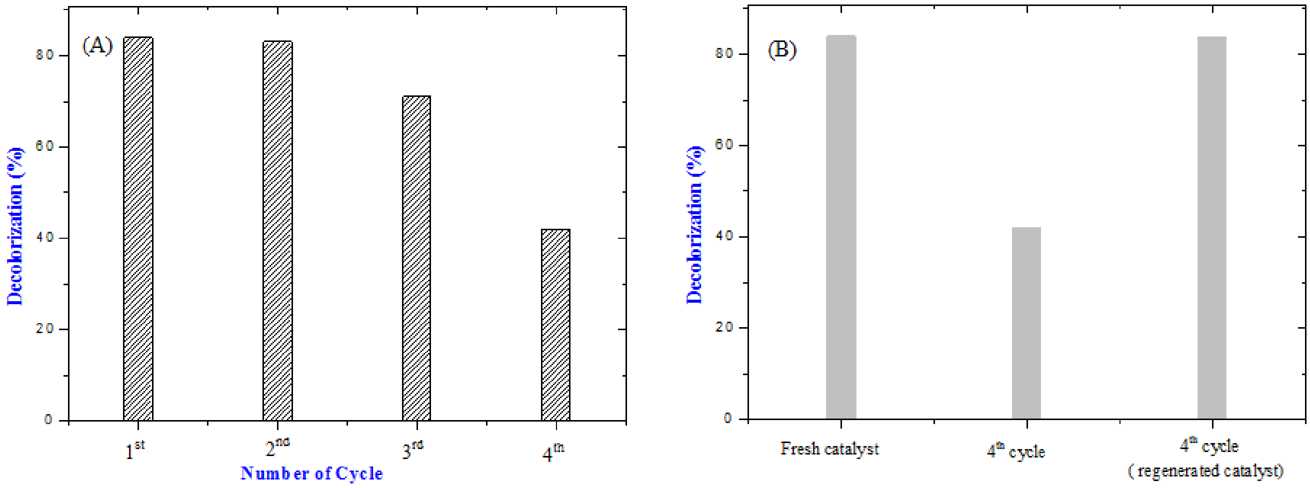

Fig. 10. (A) Effect of recycle number the catalyst 5 Cu-clay on the oxidation of Methyl Orange , (B) comparative results of the removal efficiencies of MO by the 5Cu-clay in the 1st and 4th cycles without regeneration, and that of the 4th cycle obtained by employing the regenerated catalyst after the 3rd run via mild acid wash.

IV. CONCLUSION

In this work, the decolorization of MO in aqueous solution by CWPO process has been studied on different experimental conditions, including different pH value of solutions, dosages of H_2O_2 and Cu, temperature. The best operation parameters for the Fenton oxidation of MO were 5 wt.% of copper ions loading, 4.0 g/L of catalyst dosage, and 2,5ml of H_2O_2 for 15 mg/L initial MO concentration at an initial pH 7 with 25°C temperature. Under these conditions, 94% decolorization efficiency of MO in aqueous solution was achieved within 120 min of reaction time. In addition, it was found that the decolorization efficiency of MO enhanced with the increasing of reaction temperature.

The powder diffraction patterns of the Cu-Clay catalysts verified that the copper oxide was formed by impregnating copper salt in Clay matrix. The SEM/EDX observation also identified the copper oxides were well dispersed and the copper was binding in the clay matrix.

Cu-clay is a highly efficient catalyst for MO oxidation, which is reusable and highly active under ambient conditions without the addition of other oxidants. It was possible to regenerate the deactivated catalyst by washing with weak acid giving almost the same activity compared to that of the fresh catalyst. Nevertheless, other regeneration methods may be suitable to maintain the high catalytic activity in the long run.

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