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Copper Oxide Incorporated Zeolite Catalyst Developed from Waste Coal Fly Ash Material and Its Catalytic Wet Peroxide Oxidative Degradation of Crystal Violet Dye

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ABSTRACT

CuO incorporated highly efficient and cheap catalyst material zeolite (CuO/FAZ) was synthesized from waste coal fly ash by ion exchange followed by calcination process. All the synthesized materials were characterized by various techniques. Catalytic wet peroxide oxidation using CuO/FAZ as a heterogeneous catalyst was investigated in the degradation of crystal violet (CV) dye in aqueous solution with H_2O_2 oxidant. CuO/FAZ significantly had high efficiency in the degradation of CV (100%), and 100 mg catalyst was sufficient to degrade 50 mg/L dye at pH 6.8 after 180 min treatment. CuO loading, catalyst dosage, oxidant concentration, dye concentration, solution pH and recycling of the catalyst were investigated in order to evaluate Fenton effects. These results indicated that the catalyst had a superior activity in the degradation and mineralization of dye. Further, the catalyst was highly reusable and stable for long-running wet catalytic application.

1. Introduction

Wastewaters polluted with dyes and pigments are discharged from many industrial units, which are hazardous and have the potential to harm aquatic life and the environment. Around 128 tons of different synthetic dyes are released daily and 7x10^5 tons of dye stuffs are produced annually to the global environment [1]. Increased demand for textile products and the increase in their production coupled with the use of synthetic dyes have together contributed to dye effluent becoming one of the significant sources of severe water pollution problems in recent times [1, 2]. Crystal violet (CV), a triphenylmethane dye, is extensively used in textile dyeing, paper printing, leathering, as a staining agent in bacteriological and histopathological applications, and as a dermatological agent [2, 3]. It is highly toxic and mutagenic, and in aqueous system decreases light penetration and photosynthetic activity, causing oxygen deficiency and limiting downstream beneficial uses such as recreation, drinking water and irrigation [2-4]. Environmental pressures have impelled to develop new and powerful technologies for the degradation of triphenylmethane dyes from aqueous medium to avoid their dangerous environmental accumulation. Several technologies are currently used for removal of dyes such as coagulation/flocculation, membrane processes, adsorption, biological treatment, chemical oxidation, but many of them are expensive or generate bulky sludge [1, 3, 5].

Advanced oxidation processes (AOPs) involve the formation of hydroxyl radicals that attack all types of inorganic and organic pollutants in wastewater [6, 7]. Among AOPs, catalytic wet peroxide oxidative degradation (CWPO) has the potential for widespread use in treating wastewater when compared to other degradation systems. CWPO is a more efficient and environmental - friendly technique for destruction of dyes by the action of hydroxyl radicals ($OH^{\cdot}$) [7, 8]. Furthermore, the performance of CWPO process may be greatly improved if heterogeneous catalyst is employed. Major advantage of the heterogeneous catalytic material is its easy recovery. Unlike homogeneous system, this heterogeneous catalyst can be recuperated by means of a simple operation and reused in the next runs. Another one important notable point is the minimal leaching of active species under the reaction conditions and there is no discharge of sludge to the environment [8, 9].

Fly ash (FA) is a significant by-product of coal thermal power generation and its predominant disposal route is landfill or dumping at sea. Utilization of this waste residue is possible and various routes, including the manufacture of cement, concrete, ceramics, zeolites and adsorbents have been documented. Among the high value applications of FA, its use as a catalyst and catalyst support is of paramount importance. Silica and alumina are the major components of fly ash. It is perhaps not surprising that a number of studies have investigated the application of fly ash in the preparation of zeolites [10-12]. For the purpose of improvement of CWPO of CV dye, in the present work fly ash converted zeolite is modified with copper oxide incorporation.

A wide number of studies have been reported in literature describing the incorporation of Cu species over different inorganic supports, such as zeolites (synthesized from chemical precursors and natural sources [13-15], silica [16, 17], alumina [18] and mesostructured materials [19]. To our best knowledge, no investigation has been reported on CuO incorporated fly ash zeolite for activation of H_2O_2 in CV degradation. With this view we have undertaken a detailed study on the CWPO of CV dye in aqueous solution. The reaction conditions were varied to investigate the effect of CuO loading, dye concentration, catalyst dosage, H_2O concentration and pH.

2. Experimental Methods

2.1 Materials

The fly ash (FA) used in this study was collected from electrostatic precipitators of Tuticorin (Tamil Nadu) thermal power plant. Double distilled water was used in all cases for preparing solutions. Crystal violet dye was purchased from Rankem, India. All other chemicals, NaOH, sulphuric acid (LOBA chemie, India), cupric sulphate, hydrochloric acid, potassium dichromate, ferrous sulphate (all from Merck, Mumbai), silver sulphate (Qualigens Fine Chemicals, Mumbai), Ferroin indicator (Rankem, India) were of chemically pure and guaranteed reagents. pH of the dye solution was adjusted with aqueous HCl and NaOH solutions.

2.2 Synthesis of Zeolite NaX (FAZ)

The synthesis process involves alkali fusion and hydrothermal treatment [10, 12] and is given below. The received fly ash (FA) particles were sieved through 75- mesh screen (75 µm) to eliminate large particles. Then it was treated with acid (HCl) to facilitate fly ash zeolization. Finally, it was thoroughly washed with DD water and filtered, dried at 100 °C for overnight prior to use. The acid treated FA was mixed with sodium hydroxide at 1:1.3

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ratio (wt/wt) and fused at 550 °C for 1 h. Thereafter, the fused product was mixed with DD water, and the resulting slurry was aged for 20 h and finally crystallized at 90 °C for 6 h. After synthesis, the resultant solid product was recovered by filtration and washed several times with DD water until the pH of the samples was about 9. Then the sample FAZ was filtered and dried.

2.3 Synthesis of CuO/FAZ

About 3 g of FAZ was dispersed in 100 mL of 0.1 M cupric sulphate solution and was continuously stirred for 20 h. The obtained Cu^{2+} incorporated FAZ was filtered through whatman No.1 filter paper, washed thoroughly with DD water till the filtrate was free from Cu(II) metal ions. Then it was dried at 100 °C overnight. Finally, the sample was calcined at 450 °C for 4 h, in order to obtain CuO incorporated fly ash converted zeolite. The synthesized material was labeled as CuO/FAZ.

2.4 Material Characterization

Mineralogical analysis of the synthesized catalysts was conducted by the use of a Philips X'Pert Pro- MPD X-ray diffractometer with Cu-K_α radiation (λ = 1.5406 Å) at 40 kV and 30 mA by scanning the samples from 10 to 80°. Thermogravimetric analysis was performed using TGA7 (Perkin Elmer), Q500 Hi Res TGA instrument in the range of 50 to 800 °C with a temperature rise of 10 °Cmin^{-1} in N_2 atmosphere. Morphological analysis of the solid samples was conducted by the use of Scanning Electron Microscope (VEGA 3 TESCAN). UV-visible spectra of the degraded solution of crystal violet were obtained in the wavelength range 500-800 nm on Perkin-Elmer spectrophotometer, Lambda 25 model.

2.5 Catalytic Wet Peroxide Oxidative Degradation of CV

Catalytic oxidative degradation of CV dye was carried out in ambient condition with flat bottom three necked reactor containing 200 mL of the dye (50 ppm), at natural pH (6.8), H_2O_2 (10 mL/L), appropriate catalyst load (100 mg) and stirrer speed of 320 rpm for fixed time interval (20 min). Before oxidation, i.e., prior to the addition of H_2O_2 the suspension was magnetically stirred for about 30 min to establish the adsorption/desorption equilibrium between dye and the catalyst. Then H_2O_2 was added and the degradation of CV was commenced. After every 20 min time interval, the mixture was centrifuged and the supernatant was estimated spectrophotometrically at λ_{max} value of 588 nm. Percentage degradation of CV was calculated using Eq. (1)

$$\text{Degradation \%} = \frac{(A_o - A_t)}{A_o} \times 100 \qquad (1)$$

Where A_o and A_t are the initial and time t dye sample absorbance, respectively. According to the Beer-Lambert's law A_o and A_t are proportional to C_o and C_t, which are the initial and time t concentrations of CV dye respectively. The wet catalytic oxidative degradation of CV with CuO/FAZ was examined for the influence of various reaction parameters like CuO loading on FAZ, catalyst dose, H_2O_2 concentration, initial concentration of CV and pH. The degradation experiment was repeated five times with the same CuO/FAZ catalyst under optimized condition to test its stability on reuse.

Reduction in COD load of the reaction mixture was monitored during the oxidation reaction by the open dichromate reflux method [20]. In this method, 10 mL of the reaction mixture was mixed with 25 mL of 0.0147 M $K_2Cr_2O_7$ reagent, 35 mL conc. H_2SO_4 and a pinch of silver sulphate. The mixture was refluxed for 2 h, cooled and titrated with 0.05 M ferrous-ammonium sulphate (FAS) solution using ferroin indicator. The whole procedure was repeated with a blank taking 10 mL of distilled water in place of the reaction mixture. COD was computed from formula given in Eq. (2).

$$\text{COD (mg/L)} = \frac{(A - B) \times M \times 8000}{V} \times 100 \qquad (2)$$

where B = volume of FAS used for Blank titration, A = volume of FAS used for sample titration, M = Molarity of FAS, V = Volume of the reaction mixture. The COD change/decline in % is calculated by the formula in Eq. (3)

$$\%\,\text{COD} = \frac{(\text{COD}_o - \text{COD}_t)}{\text{COD}_o} \times 100 \qquad (3)$$

where COD_o = COD of the reaction mixture at t = 0 (i.e. before commencement of oxidation) and COD_t = COD of the reaction mixture at t = t (i.e. after oxidation proceeded for time, t).

3. Result and Discussion

3.1 Material Characterization

3.1.1 XRD Studies

The X-ray diffraction (XRD) patterns of FA, FAZ and CuO/FAZ are shown in Fig. 1. Based on the XRD pattern of FA (Fig. 1a), the main mineral phases determined are quartz (SiO_2) and Mullite ($3Al_2O_3.2SiO_2$) [10]. Fig. 1b shows that a pure zeolite NaX (FAZ) crystalline phase has been obtained from FA and it is perfectly matching with JCPDS No. 39-0218 [12]. This XRD pattern contains none of the mineral phases observed in Fig. 1a. Fig. 1c clearly indicates the presence of CuO into the zeolite framework and the presence of all CuO peaks at 2θ = 28.0, 35.5, 38.7 and 48.7° matchable with those of monoclinic CuO (JCPDS No. 05-0661) [13-16]. The marking difference of CuO/FAZ pattern (Fig. 1c) from other (Fig. 1a and b) is that the former has only broad signals characteristic of amorphous structure while the latter two display many sharp high intense signals indicating the presence of only crystalline structures. From both XRD and SEM data (Fig. 2), it is interesting to note that FAZ with high crystallinity is observed. But after CuO incorporation, it is converted into amorphous form. This result clearly demonstrates the loading of CuO in nano amorphous form over crystalline zeolite framework. A similar observation was reported on the CuO/nanozeolite X catalyst [15]. The average crystallite sizes (D) (Scherrer method) of the materials are PFA = 64.73 nm, FAZ = 51.84 nm and CuO/FAZ = 57.13 nm.

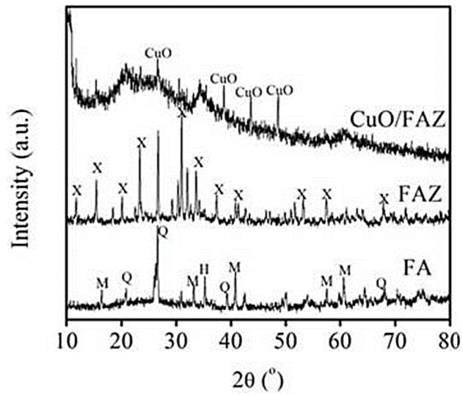

Fig. 1 XRD patterns of (a) FA, (b) FAZ and (c) CuO/FAZ

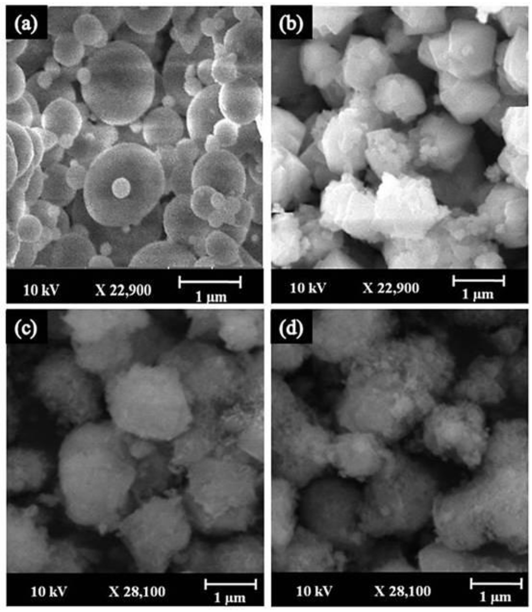

Fig. 2 SEM images of (a) FA (b) FAZ (1 µm) (c) CuO/FAZ (1 µm) and (d) CuO/FAZ (spent)

3.1.2 SEM and EDX Studies

The SEM images of FA, FAZ, CuO/FAZ and CuO/ FAZ (spent) samples are shown in Fig. 2. FA sample (Fig. 2a) has perfectly spherical and smooth – surfaced grains of varying size (submicron-micron). However, FAZ (Fig. 2b) displays almost uniform-sized (1-2 µm) grain like crystals with irregular shape and surfaces [12]. The SEM micrographs thus indicate that in comparison to the parent fly ash, FAZ has undergone significant changes in the surface topography. It is also notable in FAZ image b that the bigger

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zeolite particle comprises many smaller spherical aggregate particles. CuO/FAZ (Fig. 2c) has irregular shaped and sized but still bigger (> 2 μm) particles. A close examination of the image of CuO/FAZ reveals the existence of nano fringes (small densely arranged fibre like structure) on the entire surface of FAZ particles. After degradation of CV (Fig. 2d), CuO/FAZ (spent) catalyst does not undergo change in the morphology of original CuO/FAZ catalyst. The presence of 22.39 atomic % of Cu from EDX analysis confirms the formation of CuO particles over FAZ.

3.1.3 Thermal Studies

The thermal and the consequent structural stabilities of FAZ and CuO/FAZ materials was assessed by TGA (Fig. 3) and DTA (Fig. 4). As seen from Fig. 3a of a sharp declining thermogram, FAZ sample exhibits a continuous weight loss from room temperature upto say 400 °C with a weight loss of 23.58%. Correspondingly its DTA in Fig. 4 shows initially an endothermic (upto 50 °C) and subsequently a sharp exothermic thermogram with peak centering at 150 °C and the process extending upto 400 °C. The results of TGA and DTA of FAZ sample are thus consistent with each other. This weight loss is mainly attributable to removal of absorbed moisture and weakly bound interlayer water molecules from cavities/channels of zeolite at lower temperature (endothermic) and subsequently the removal of bulk of (23.56%) intra-zeolite water molecules [12]. CuO/FAZ, on the other hand, displays a contrasting thermogram in TGA and DTA (Fig. 3b and 4b). It shows only a meagre and gradual weight loss of 2.4% upto 650 °C and another meagre gradual weight loss of 1.7% at 650-800 °C. The first weight loss, as seen from DTA, is an endothermic while the second weight loss is an exothermic process. Evidently, inter- and intra-zeolite water elimination corresponds to first process while the small destruction/disordering of monoclinic CuO is responsible for second process [13, 15]. Anyway the entire thermal study demonstrates that CuO/FAZ is least susceptible to water elimination and thermal decomposition and is safe for heat treatment atleast upto 650 °C. In other words CuO/FAZ is thermally more stable than its precursor FAZ.

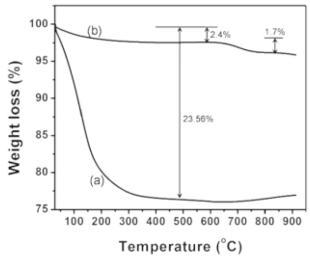

Fig. 3 TGA curves of (a) FAZ and (b) CuO/FAZ

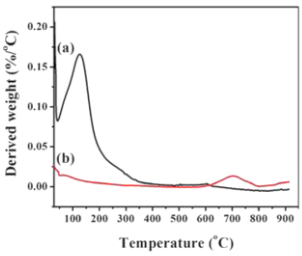

Fig. 4 DTA graphs of (a) FAZ and (b) CuO/FAZ

The three characterizations (XRD, SEM and thermal) altogether make it evident that CuO/FAZ is distinct from FAZ in terms of structure (amorphous), morphology (bigger particle with nano fringes) and thermal characteristics (least susceptible). Appearance wise also CuO/FAZ has brown color while FAZ has sandal color.

3.2 Study of Catalytic Wet Peroxide Oxidation Behavior of CuO/FAZ

3.2.1 Comparison of Adsorption and Degradation Efficiencies of FAZ, CuO and CuO/FAZ

Adsorption and degradation extent of crystal violet dye (cationic very hazardous dye) with/without catalysts of FAZ, CuO and CuO/FAZ were examined and the results are displayed in Fig. 5a. Before beginning degradation experiment of CV, adsorption experiments were carried out with FAZ, CuO and CuO/FAZ catalysts. The amounts of dye adsorption on the catalysts are 18.2% for FAZ, 0% for CuO and 0.2% for CuO/FAZ after 180 min contact time. It was demonstrated that the adsorption of CV on CuO//FAZ was extremely low.

Self-degradation experiments (H_2O_2 alone; without catalyst) showed that only 15% degradation was possible for CV dye. In contrast, remarkable improvement of CV degradation occurs with CuO/FAZ/H_2O_2 suspension and about 100% of CV is degraded in 180 min at natural pH 6.8. But FAZ and CuO exhibit 45% and 20% degradation respectively after 180 min of reaction time. These results demonstrate that the active centers are CuO sites in the zeolite structure which increases the degradation extent of the dye.

3.2.2 Effect of CuO Loading

The effect of CuO load on the degradation of CV with different CuO/FAZ catalyst was demonstrated in Fig. 5b. Four catalysts were prepared by ion exchanging of the FAZ in 0.05, 0.1, 0.5 and 1 M of Cu^{2+} aqueous solution. Dye degradation increases with the increase in CuO loading upto 0.1 M Cu^{2+} solution and thereafter the degradation % decreases. At high CuO loading, particles may tend to aggregate which reduces the surface area of the catalyst, and hence it decreases the number of active sites present on the catalyst for the degradation of CV [15]. Hence, the production of less hydroxyl groups accounts well for low catalytic activity. All further studies were done with CuO/FAZ catalyst where CuO was loaded using 0.1 M $CuSO_4$ solution which is found optimal.

3.2.3 Effect of Dye Concentration

The effect of dye concentration on the percentage degradation of CV is shown in Fig. 5c. When the concentration of CV is varied from 20 ppm to 100 ppm, the percentage degradation of CV is decreased from 100 to 84%. With a further increase of CV concentration to 200 ppm, the time for complete degradation of CV is increased from 180 min to 360 min. As seen from Fig. 5c, 100% degradation is observed for 50, 40 and 20 ppm at/below 180 min. Therefore 50 ppm CV concentration is optimal and is used for further variation study.

3.2.4 Effect of H_2O_2 Concentration

The effect of H_2O_2 concentration on the percentage degradation was investigated at different concentration of H_2O_2 (in the range of 2.5 to 25 mL/L). As can be seen from Fig. 5d, increase in H_2O_2 concentration from 2.5 mL to 10 mL represents an enhancement of the % degradation of CV (increased from 55% to 100% within 180 min). This arises because more H_2O_2 would accelerate the reaction between H_2O_2 and catalyst, and thus more hydroxyl radicals are generated [21]. However, further increase in H_2O_2 concentration from 10 mL to 25 mL/L decreases the % degradation from 100% to 60% significantly because of the scavenging effect of $OH^{\bullet}$ by H_2O_2. Hydroxyl radical reacts with excess H_2O_2 to produce hydroperoxy (${}^{\bullet}OOH$) and superoxide anion ($O_2^{\bullet -}$) according to the Eq. (4) [22].

$$H_2O_2 + {}^{\bullet}OH \xrightarrow[-H_2O]{} HOO^{\bullet} \xrightarrow{+{}^{\bullet}OH} O_2 + H_2O \quad (4)$$

Therefore, the optimal H_2O_2 concentration is 2 mL for 200 mL dye.

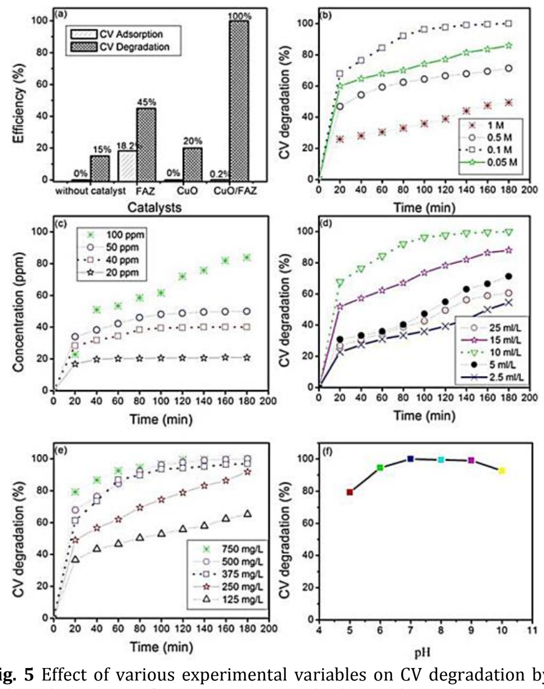

Fig. 5 Effect of various experimental variables on CV degradation by CuO/FAZ; (a) Effect of various catalysts (H_2O_2 = 10 mL/L, 500 mg/L catalyst, 50 ppm dye, pH = 6.8); (b) Effect of CuO loading (H_2O_2 = 10 mL/L, 500 mg/L catalyst, 50 ppm dye, pH = 6.8); (c) Effect of dye concentration (H_2O_2 = 10 mL/L, 500 mg/L catalyst, pH = 6.8); (d) Effect of H_2O_2 concentration (500 mg/L catalyst, 50 ppm dye, pH = 6.8); (e) Effect of catalyst dosage (H_2O_2 = 10 mL/L, 50 ppm dye, pH = 6.8); (f) Effect of pH (H_2O_2 = 2 mL, 500 mg/L catalyst, 50 ppm dye)

3.2.5 Effect of Catalyst Loading

The effect of catalyst loading on the percentage degradation of CV is shown in Fig. 5e. The influence of catalyst loading on % degradation was investigated at different catalyst loading (in the range of 750, 500, 375, 250 and 125 mg/L). As can be seen, maximum dye degradation of 100% is observed at 500 mg/L followed by 99.8% at 375 mg/L, 91.8% at 250mg/L and 65% at 125 mg/L in 180 min duration [23, 24]. It is clear that the highest degradation efficiency is achieved at the highest catalyst dosage, mainly because increasing catalyst dosage could increase the active sites. Therefore the optimal catalyst load is 500 mg/L.

3.2.6 Effect of pH

pH is one of the important factors in heterogeneous Fenton like reaction. The effect of initial pH value on the degradation of CV with CuO/FAZ catalyst was determined over a pH range from 5 to 10 as presented in Fig. 5f. The % degradation at pH 5, 6, 7, 8, 9 and 10 is 69, 94, 100, 99.4, 99 and 92.6% respectively for 180 min. Increase in the pH (under alkaline condition) favours high degradation, which may be due to the formation of reactive hydroxyl species on the surface of the catalyst [25].

3.3 Degradation Pathway

The combination of CuO and FAZ results in a synergic effect in catalytic activity, (as evident from Fig. 5a and the corresponding discussion) suggesting that the dispersive CuO is capable of reacting with hydrogen peroxide producing $OH^{\cdot}$. The heterogeneous activation of H_2O_2 can be expressed in the following Eqs. 5, 6 and 7.

Oxidation-reduction reactions between Cu(II)/Cu(I) take place in the presence of excessive hydrogen peroxide forming reactive hydroxyl radicals ($OH^{\cdot}$) and hydroperoxyl ($HOO^{\cdot}$) radicals. These hydroxyl radicals attack the CV dye to give several intermediate products. Finally, CV dye is completely degraded to CO_2 and water [26, 27].

$$Cu^{2+} + H_2O_2 \longrightarrow Cu^{+} + HO_2^{\bullet} + H^{+} \quad (5)$$

$$Cu^{+} + H_2O_2 \longrightarrow Cu^{2+} + HO^{\bullet} + OH^{-} \quad (6)$$

$$\text{Dye} + HO^{\bullet} \longrightarrow [\text{dye}\,(OH^{\bullet})] \longrightarrow \text{Oxidation products} \longrightarrow CO_2 + H_2O \quad (7)$$

3.4 Reusability Study

The recyclability of catalyst is a very important factor and is based on the stability of the catalyst. The stability and reusability of CuO/FAZ catalyst was evaluated by successive five run reusability tests (Fig. 6a). Each time the catalyst was washed with water and dried at 100 °C, before reuse. After recycling four times, there was only a minor change in the degradation efficiency. This may be attributed to the attachment of dye intermediates (unremovable by water washing) on the surface/pores. This indicates that the catalyst is more stable and could easily be reused which is favorable for the potential environmental applications.

In addition, SEM images of fresh and used catalyst were studied (Fig. 2c and 2d). As can be seen, the SEM images for the fresh and used catalyst are similar to each other. For this reason, the catalyst is reusable for more runs without losing its activity.

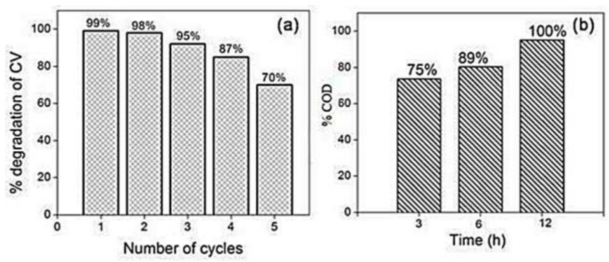

Fig. 6 (a) Reusuability study of CuO/FAZ; (b) % COD Vs time (H_2O_2 = 10 mL/L, 500 mg/L CuO/FAZ, 50 ppm dye, pH = 6.8, ambient condition)

3.5 Mineralization of Dye

Compared with degradation, mineralization of the dye (completely oxidized to CO_2 and H_2O) is more important from the view point of environmental protection. The % COD of the reaction mixture after CV degradation over CuO/FAZ (optimal conditions H_2O_2 = 2mL, 500 mg/L catalyst, 50 ppm CV, pH = 6.8, ambient condition) is 75% for 3 h, 89% for 6 h, 100% for 8 h (Fig. 6b). The high percentage of COD indicates complete mineralization of dye intermediates converted to CO_2 and H_2O.

4. Conclusion

In this work, the cheap and waste material coal fly ash (FA) is converted into zeolite (FAZ) and CuO is incorporated to design new heterogeneous Fenton catalyst (CuO/FAZ). XRD and SEM-EDX characterizations confirm the formation of CuO/FAZ catalyst. TGA and DTA studies demonstrate the much improved thermal stability of CuO/FAZ than FAZ. Hence, CuO/FAZ is an effective Fenton catalyst for generating hydroxyl radicals in the presence of H_2O_2 to degrade CV. It has synergic and better wet catalytic activity in degrading CV than FAZ and CuO. From environmental and economic point of view, CuO/FAZ is an ecofriendly, non-hazardous, cost effective, high efficient and reusable catalyst.

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