High degree Fenton-like catalytic activity of CuO/zeolite X catalyst from coal fly ash in mineralization of Indigo Carmine dye

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ORIGINAL RESEARCH ARTICLE

ABSTRACT

In this study, a new heterogeneous Fenton-like catalyst CuO/zeolite X was developed from the waste material coal fly ash initially by zeolization followed by ion exchange with Cu²⁺, precipitation with NaOH and subsequent calcination. Wet catalytic degradation of Indigo carmine (IC) dye in aqueous solution was investigated over CuO/zeolite using hydrogen peroxide oxidant. Considering that individual component zeolite or CuO had very less catalytic efficiency, the combined CuO/zeolite catalyst exhibited significantly high efficiency demonstrating synergism in the activity. Special attention was paid to the effect of CuO loading, effect of H₂O₂ concentration, dye concentration, catalyst dosage and pH on the degradation of IC dye. Complete decolorization (100%) of IC was achieved in 180 min at its natural pH of 6.5, catalyst load of 0.5 g/L and the concentration of H₂O₂ and IC at 5 mL/L and 100 mg/L respectively. The catalyst retained about 80% of its initial activity even after five runs with good stability. Hence, the catalyst was highly efficient for the Fenton degradation and mineralization of Indigo carmine dye under ambient condition.

KEYWORDS
copper oxide; Fenton activity; heterogeneous catalysis; indigo carmine; zeolite

1. INTRODUCTION

Pollution of water by dyes from different industries (e.g., textile, paper and pulp, tannery, dye and dye intermediate, Kraft bleaching etc.,) is a serious problem in the developed countries. The World Bank estimates that almost 20% of global industrial water pollution comes from the treatment and dyeing of textiles (Husain, 2010). The discharge of intense coloured wastewater into the water bodies/ecosystem poses environmental problems like aesthetic pollution (even a small amount of dye is clearly apparent), health hazards, and perturbation of aquatic life (Singh and Arora, 2011). The dyes are carcinogenic and mutagenic and can cause severe damage to human beings, such as dysfunction of brain, liver, kidney, reproductive system and central nervous system (Husain, 2010; Singh and Arora, 2011). Among the most applied dyes, indigo carmine (3,3'-dioxo-2,2'-bis-indolyden-5,5'-disulfonic acid disodium salt) or acid blue 74 (C. I. No. 73015, CAS No. 860-22-0) is a well-known anionic dye (molecular formula: C₁₆H₈N₂Na₈O₈S₂, MW: 466.35 g/mol). Its major industrial application is the dyeing of clothes (blue jeans) and other blue denim (Othman et al., 2007). Apart from its use as a textile coloring agent, it is also used as redox indicator in titration, additive in pharmaceutical tablets and capsules, medical diagnostic purposes, biological stain etc., (Barka et al., 2008). The disposal of wastewater containing indigo carmine (IC) is of environmental concern since it is a highly toxic dye that may lead to tumours at the site of application, causes skin or eye irritation, and permanent injury to cornea and conjunctiva, and can be fatal if consumed (Costa and Prado, 2009; Oliveira et al., 2011; Hammami et al., 2012). Therefore, the removal of IC from aqueous solution/wastewater is a need of the highest order. Different methodologies such as adsorption (Lakshmi et al., 2009), biological...
processes (Li et al., 2015), coagulation/flocculation processes (Allegre et al., 2004), electro-Fenton, photoelectro-Fenton processes (Flox et al., 2006) etc., have been undertaken for degradation of IC dye. However, the advanced oxidation process (AOP) (Singh et al., 2016), especially the catalytic wet hydrogen peroxide oxidation (CWPO) remains an environment-friendly and innovative technology for the treatment of wastewater containing synthetic dyes (Tehrani-Bagha et al., 2016). Fenton-like processes are used as powerful tools for the generation of hydroxyl radicals (•OH) from hydrogen peroxide which can attack organic pollutants leading to progressive degradation and complete mineralization (Nidheesh et al., 2013). Hydrogen peroxide is a powerful and environment-friendly oxidant. It can effectively break down the conjugated double bonds of dye chromophore and other functional groups such as the complex aromatic rings of dyes, thus destroying the color of the effluents (Ribeiro et al., 2016).

Considering the homogeneous Fenton process, there are few important drawbacks to be considered namely, the precipitation of metal salts at the end of the reaction and difficulty in catalyst recycling (Munoz et al., 2016; Bradu et al., 2010). As far as heterogeneous processes are concerned, most of the researchers have developed individual heterogeneous catalyst such as copper oxide, cobalt oxide etc., which usually tends to aggregate during the catalytic operation due to high surface energy, leading to the decrease of catalytic activity (Rodriguez et al., 2010). To overcome this problem, heterogeneous Fenton type catalysts on some support materials are considered (Alvarez et al., 2002; Massa et al., 2005; Melero et al., 2009; Liou and Chen, 2009). In this respect, zeolite as a support material for hosting metal oxide Fenton catalysts has drawn remarkable attention in the field of catalysis because such catalysts do not have any metal leaching and can be easily separated from the reactants/products through easy filtration. Only few studies have contributed to the synthesis of transition metal oxide (copper oxide) incorporated zeolite from chemical precursors and its application to photodegradation (Nezamzadeh-Ejhieh and Hushimaard, 2010; Nezamzadeh-Ejhieh and Amiri, 2013; Nezamzadeh-Ejhieh and Shamsabadi, 2014; Jalil et al., 2013). Hence the present work focuses on the development of CuO incorporated zeolite from the waste material coal fly ash (CuO/FAZ) and its application to wet catalytic peroxide oxidation of IC dye.

In our previous work, CuO/FAZ heterogeneous catalyst was synthesized, characterized and studied for its catalytic performance in the cationic dye crystal violet degradation with H2O2 oxidant (Subramanian and Subbulekshmi, 2016). However, so far the degradation of an anionic dye was not investigated. Hence, the present work was undertaken and this paper focuses mainly on three aspects (i) evaluation of adsorption and catalytic wet peroxide oxidative degradation performance of CuO/FAZ toward the anionic dye indigo carmine (IC) (ii) investigation of the influence of different experimental parameters like initial dye concentration, pH, peroxide concentration, CuO loading and catalyst dosage and (iii) study of the intermediate products, mechanism of the oxidation of IC dye in the Fenton process and the mineralization degree of IC dye by COD measurement.

2. MATERIALS AND METHODS

2.1. Materials

The fly ash (FA) used in this study was collected from electrostatic precipitators of Tuticorin (Tamil Nadu) thermal power plant. Indigo carmine (IC) dye (Table 1) was purchased from Loba Chemie, India as commercially available dye and used without further purification. Hydrogen peroxide (30%, w/v as an oxidant) was purchased from Merck, Mumbai. All other chemicals, NaOH, sulphuric acid (LOBA Chemie, India), cupric sulphate, hydrochloric acid, potassium dichromate, ferrous sulphate (all from Merck, Mumbai), Ferroin indicator (Rankem, India) were chemically pure and guaranteed reagents. The pH of the dye solution was adjusted with aqueous HCl and NaOH solutions. Double distilled water was used throughout this work.

Table 1. Physical properties of indigo carmine (IC) dye
2.2. Synthesis of zeolite NaX (FAZ) and CuO/FAZ

Fly ash converted zeolite (FAZ) was synthesized by alkali fusion followed by hydrothermal treatment as described in our previous work (Subramanian and Subbulekshmi, 2016). FAZ was then subjected to ion exchange process using 0.1 M cupric sulphate solution followed by precipitation with NaOH and calcination at 450°C for 4 h in order to prepare CuO/FAZ which is similar to the synthesis procedure followed in our previous work.

2.3. Material characterization

Powder X-ray diffraction (XRD) patterns were recorded for the angle 2θ = 10 - 80° in a step of 0.05° in a continuous scanning mode using the instrument, PANalytical Expert Pro-MPD with CuKa radiation (λ = 1.5406 Å) from a generator set at 30 mA and 40 KV. The specific surface area of the powder samples was determined by BET (Brunauer–Emmett–Teller) and Langmuir nitrogen adsorption/desorption method in Micromeritics ASAP 2420 surface area analyzer. SEM (Scanning Electron Microscope) images of the samples were obtained with VEGA 3 TESCAN microscope. UV-visible spectra of the degraded solution of IC dye were obtained in the wavelength range 200-800 nm on Perkin-Elmer spectrophotometer, Lambda 25 model. The oxidized products of IC dye were analyzed by Alliance 2795 HPLC coupled with a Waters Micromass Quatro triple quadrupole mass spectrometer equipped with electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) probes having mass range up to 4000 amu in quadrupole and 20000 amu in TOF.

2.4. Degradation of IC dye

Oxidative degradation of IC dye was carried out at ambient condition. In a typical experiment, 100 mg of CuO/FAZ catalyst powder was dispersed in 200 mL IC solution (100 mg/L). The reaction was conducted in a three necked flat bottom flask with constant stirring at around 300 rpm. The flask was covered and wrapped with aluminum foil to block the incidence of indoor light on the reaction mixture. At the natural pH 6.5 (prior to the addition of H₂O₂) the suspension was magnetically stirred for about 30 min to establish the adsorption/desorption equilibrium between dye and catalyst. Then, a certain amount of H₂O₂ (1 mL of 30% w/v) was added to the above suspension under continuous magnetic stirring. At given time intervals (20 min), 1 mL aliquot was withdrawn from the reaction solution, and immediately centrifuged to remove the catalyst and for subsequent analysis of dye solution. The degradation was monitored by UV-Visible spectroscopy at 608 nm, the maximum absorption wavelength of IC and its percentage was calculated using Eqn. (1),

\[
\text{Degradation } \% = \frac{(A_o - A_t)}{A_o} \times 100
\]

where \(A_o\) is the initial absorbance of dye and \(A_t\) is the absorbance at selected time intervals.

The catalytic degradation of IC was investigated for the influence of experimental variables like CuO loading on FAZ, catalyst dosage, H₂O₂ concentration, initial concentration of IC and pH. For the recycle runs of catalyst, the used catalyst was collected by centrifugation, washed with water, dried at 100°C and reused for IC degradation. This was repeated for several cycles of the degradation experiment. Reduction in the COD (Chemical Oxygen Demand) load/value of the reaction mixture was monitored during the degradation reaction by the open dichromate reflux method (Subramanian and Subbulekshmi, 2016).

3. RESULTS AND DISCUSSION

3.1. Materials characterization

3.1.1. XRD studies

The X-ray diffraction (XRD) patterns of Cu exchanged FAZ, CuO/FAZ and bulk CuO (the inset of Figure 1) are shown in Figure 1. In the XRD pattern of pristine CuO (inset Figure 1) characteristic lines appeared at 2θ = 32.5, 35.5, 38.7, 48.7, 53.4 and 58.3° (JCPDS No. 05-0661) which indicate monoclinic crystalline phase (Nezamzadeh-Ejhieh and Shamsabadi, 2014; Hao et al., 2006). As evident from Figure 1, after exchange of Cu²⁺ ions during ion exchange process, the characteristic peaks of FAZ were not changed (Singh et al., 2016). In the XRD pattern of CuO/FAZ some new peaks were observed at 2θ = 28.0, 35.5, 38.7, 48.7, 53.4 and 58.3° (JCPDS No. 05-0661) which indicate monoclinic crystalline phase (Nezamzadeh-Ejhieh and Shamsabadi, 2014; Hao et al., 2006). As evident from Figure 1, after exchange of Cu²⁺ ions during ion exchange process, the characteristic peaks of FAZ were not changed (Singh et al., 2016). In the XRD pattern of CuO/FAZ some new peaks were observed at 2θ = 28.0, 35.5, 38.7 and 48.7° which indicate the formation of CuO incorporated FAZ (Nezamzadeh-Ejhieh and Shamsabadi, 2014). During calcination process, some peaks of FAZ disappeared and intensity of some peaks decreased. In addition, XRD results clearly shows the presence of CuO with low intense and broad signals, indicating low degree of crystallinity for FAZ and nano features for CuO. This may be attributed to the CuO loading inside the channels/cavities/pores of FAZ and partial blocking of
surrounding zeolite framework (Nezamzadeh-Ejhieh and Shamsabadi, 2014; Hao et al., 2006; Subramanian and Subbulekshmi, 2016). Nezamzadeh-Ejhieh and Hushmandrad (2010) showed that by incorporation of CuO into the nano zeolite X, the intensity of peaks significantly decreased with respect to those of the nano zeolite (NX). Similar observation on CuO/FAZ was made by Nezamzadeh-Ejhieh et al. (2014) for CuO incorporated nano zeolite X. Similar observation on CuO incorporated MCM-41 was also made by Hao et al. (2006).

Figure 1. XRD patterns of (a) Cu exchanged FAZ and (b) CuO/FAZ (inset: CuO).

3.1.2. Surface area characterization
The surface area, pore diameter and pore volume of FAZ and CuO/FAZ were studied by BET N₂ adsorption/desorption (Figure 2). BET surface area of the synthesized materials CuO/FAZ and FAZ were 58 m²/g and 413 m²/g respectively. This clearly indicates that the surface area of CuO/FAZ was considerably less than that of FAZ, which may be attributed to the occupation of zeolite pores/channels/cavities by CuO nano particles and partial blocking of surrounding zeolite framework (Nezamzadeh-Ejhieh and Shamsabadi, 2014; Hao et al., 2006; Subramanian and Subbulekshmi, 2016). Further the total pore volume was decreased with the incorporation of CuO in FAZ.

3.1.3. SEM studies
The surface morphology of FAZ, Cu exchanged FAZ, CuO/FAZ, pristine CuO and CuO/FAZ (spent) was studied by SEM and the images are shown in Figure 3. Close examination of the SEM image (Figure 3a) indicates that the FAZ has spherical grain like crystals of diameter 5 µm. The image, Figure 3b shows undefined shape indicating the formation of agglomerate coarse Cu-exchanged FAZ flakes. The image of CuO/FAZ (Figure 3c) coincides with the image of FAZ in Figure 3a showing spherical grains. This similarity definitely indicates that FAZ was not affected by CuO incorporation. Pristine CuO has capsule like structures in nano dimension (Figure 3d). Further, appearance of similar images for fresh (Figure 3c) and spent CuO/FAZ catalyst (Figure 3e) reveals that catalyst is chemically stable and the morphology was not affected by its catalytic role in dye degradation.

3.2. Study of catalytic wet peroxide oxidative degradation of IC

3.2.1. Comparison of adsorption and degradation efficiencies of FAZ, CuO and CuO/FAZ
The catalytic activity of CuO, FAZ and the role of H₂O₂ in the oxidative degradation of IC was investigated.

Figure 2. BET isotherms of (a) FAZ and (b) CuO/FAZ
The reaction was carried out in the presence of catalyst or $\text{H}_2\text{O}_2$ alone or both (Figure 4a). In Figure 4a, the plain portion represents the activity of catalyst alone (without $\text{H}_2\text{O}_2$) and corresponds to IC adsorption. The shaded portion represents the activity of catalyst in the presence of $\text{H}_2\text{O}_2$ and the resultant ‘OH formation. Hence it corresponds to degradation of IC dye, as monitored by UV VIS and LCMS spectral study. It was obvious in Figure 4a that almost no degradation occurred with the CuO/FAZ catalyst or $\text{H}_2\text{O}_2$ alone and the value was almost negligible ($\leq 4\%$ after 180 min reaction). This is attributed to the low potential to yield hydroxyl radical. Alternatively, the catalyst FAZ or CuO exhibited 45% or 38% IC degradation, respectively after 180 min reaction time while the combination of CuO/FAZ showed 100% activity at the same condition.

Also, it was noticeable from Figure 4a that FAZ or CuO individually exhibited considerable level of IC dye adsorption of 34% and 24% respectively; however, CuO/FAZ has strikingly showed low adsorption (5%). Apparently this implies that owing to suitable adsorption sites, FAZ or CuO favours IC dye adsorption; however on incorporation of CuO onto FAZ, both materials lost binding sites through their mutual interaction. Interestingly, low value of adsorption (5% for CuO/FAZ) is an advantageous feature for any catalyst because excessive adsorption sometimes hinders dye degradation and is likely to reduce the catalytic efficiency.

Figure 3. SEM images of (a) FAZ, (b) Cu exchanged FAZ, (c) CuO/FAZ, (d) pristine CuO and (e) CuO/FAZ (spent)

Figure 4. Effect of experimental variables on IC degradation by CuO/FAZ; (a) Effect of various catalysts ($\text{H}_2\text{O}_2 = 5 \text{ mL/L}$, 500 mg/L catalyst, 100 mg/L dye, pH = 6.5); (b) Effect of CuO loading ($\text{H}_2\text{O}_2 = 5 \text{ mL/L}$, 500 mg/L catalyst, 100 mg/L dye, pH = 6.5); (c) Effect of $\text{H}_2\text{O}_2$ concentration (500 mg/L catalyst, 100 mg/L dye, pH = 6.5); (d) Effect of dye concentration (500 mg/L catalyst, $\text{H}_2\text{O}_2 = 5 \text{ mL/L}$, pH = 6.5); (e) Effect of catalyst dosage (100 mg/L dye, $\text{H}_2\text{O}_2 = 5 \text{ mL/L}$, pH = 6.5); (f) Effect of pH (100 mg/L dye, $\text{H}_2\text{O}_2 = 5 \text{ mL/L}$, 500 mg/L catalyst).
3.2.2. Effect of CuO loading

The effect of CuO load on the performance of CuO/FAZ catalyst was investigated, because the loading of CuO is significant in fixing the degradation efficiency. Figure 4b shows the effect of CuO loading on the catalytic activity at the optimal condition: 500 mg/L catalyst, 100 mg/L IC, pH = 6.5 and H$_2$O$_2$ = 5 mL/L. The degradation efficiency increased with increase in CuO loading from 0.05 to 0.1 M and thereafter decreased. It seems that with increase in the amount of active species (i.e. Cu$^{2+}$), aggregation of CuO particles on zeolite could occur which leads to hinder/Hide the active sites on catalyst resulting in the loss of activity and degradation (Liou and Chen, 2009; Nezamzadeh-Ejhieh and Shamsabadi, 2014; Hu et al., 2015; Singh et al., 2016; Subramanian and Subbulekshmi, 2016). Hence, CuO load from 0.1 M Cu(II) solution for CuO/FAZ catalyst was optimal and was subsequently used for all further studies.

3.2.3. Effect of H$_2$O$_2$ concentration

In catalytic wet peroxide oxidation reaction, the concentration of oxidizing agent is an important parameter (Sun et al., 2008). Hence, the effect of initial concentration of H$_2$O$_2$ was studied by varying its concentration from 1.0 to 15 mL/L in the following optimal condition: 100 mg/L IC, pH = 6.5 and catalyst 500 mg/L. Figure 4c demonstrates that in the H$_2$O$_2$ concentration range from 1.0 to 15 mL/L, the % degradation of IC first increased up to 5 mL/L and then decreased. The maximum degradation was obtained at the H$_2$O$_2$ concentration of 5 mL/L. The initial enhancement of IC degradation is attributed to the generation of more number of hydroxyl radicals (‘OH) from H$_2$O$_2$. Similar observation was made by Dulman et al., (2012). The subsequent decrease in % degradation with higher H$_2$O$_2$ concentration is explained by the fact that the in situ formed ‘OH radical reacts with excess H$_2$O$_2$ available to give the less reactive ‘OOH species, which in turn reacts with ‘OH to form inactive oxygen molecules (Daud and Hameed, 2010; Ribeiro et al., 2016; Singh et al., 2016; Munoz et al., 2016) as shown in Eqn. (2).

\[
\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \cdot\text{OOH} + \cdot\text{OH} + \text{O}_2 + \text{H}_2\text{O}
\]  

Therefore, the optimal H$_2$O$_2$ concentration was 5 mL/L or 1.0 mL for 200 mL dye solution.

3.2.4. Effect of initial dye concentration

The effect of initial dye concentration was studied by varying the IC concentration from 25 to 200 mg/L at the optimal condition: catalyst = 500 mg/L, pH = 6.5 and H$_2$O$_2$ = 5 mL/L (Figure 4d). The extent of catalytic degradation reaches maximum at 100 mg/L dye concentration and the dye was completely (100%) degraded in 180 min. At 200 mg/L dye concentration, 110 mg/L (55%) degradation was achieved in 180 min. This is explainable by the fact that when the H$_2$O$_2$ volume is maintained constant (at 5 mL/L) and hence the hydroxyl radical concentration is also constant, but the initial concentration of dye is increased, the relative number of hydroxyl radicals attacking the dye molecules decreases (Daud and Hameed, 2010). Hence, complete dye degradation requires a longer time and a leveling effect or constancy is, therefore, maintained. However, at lower level increasing the concentration of IC dye enhances the probability of collision between dye molecules and oxidizing species, leading to an increase in % degradation (Daud and Hameed, 2010; Hu et al., 2015; Ribeiro et al., 2016; Singh et al., 2016). Hence, 100 mg/L is the optimal IC dye concentration for degradation.

3.2.5. Effect of catalyst dosage

The amount of catalyst is a crucial parameter in deciding the activity. The effect of catalyst dosage was studied by varying the amount of catalyst from 0.125 to 0.5 g/L at the optimal condition: 100 mg/L IC, pH = 6.5 and H$_2$O$_2$ = 5 mL/L. As Figure 4e shows, increasing the amount of catalyst leads to an increase in the percent degradation. For 0.5 g/L CuO/FAZ catalyst, a degradation of 83% was reached after 60 min and a maximum of 100% after 180 min. The increase in the catalyst dosage can contribute to an increase in the degree of formation of ‘OH radicals, and therefore it leads to an increase in % degradation (Catrinescu et al., 2003; Dijeffal et al., 2014; Hu et al., 2015; Ribeiro et al., 2016; Singh et al., 2016).

3.2.6. Effect of pH

The efficiency of wet catalytic degradation process strongly depends on pH of the reaction solution (Catrinescu et al., 2003). The pH of zero point charge (pH$_{zpc}$) for CuO/FAZ was determined as 7. At pH values lower than pH$_{zpc}$, the charge of the catalyst surface is positive while it is negative at higher pH. The pH was changed in the range of 4 – 10 using a few drops of 0.1 M HCl or NaOH and the effect was studied at optimal condition (Figure 4f). The pK$_a$ of the IC dye from literature is found to be 11.6 (Barka et al., 2008). Therefore, it is certain that in the range of all pH applied, the IC structure remained unchanged. At basic pH 10, 100% degradation was observed. Surprisingly,
even at pH 4, IC dye degradation proceeded at almost the same extent as at pH 10. That means IC degradation is favoured at both acidic and alkaline conditions. The degradation trend at alkaline pH could be explained by the fact that the deprotonation of H\textsubscript{2}O\textsubscript{2} in highly alkaline medium and the consequent decomposition of H\textsubscript{2}O\textsubscript{2} is quite easy to form more number of hydroxyl radical (Gemeay et al., 2003; Li et al., 2014). Similar pH effects were observed in the oxidative degradation of indigo carmine dye (Othman et al., 2007; Zaied et al., 2011; Gemeay et al., 2003).

Favourable degradation of IC dye at acidic pH 4.0 is explained as follows. Since IC is an anionic dye bearing one sulphonato group, it has negative charge even at pH 4.0. But the catalyst with pH\textsubscript{zpc} of 7.0, has positive charge at pH 4.0. Hence a strong electrostatic attraction between the dye and the catalyst could exist which helps to load the dye on the catalyst and ultimately causes a major destruction. This phenomenon is validated by the observation that at pH close to pH\textsubscript{zpc} (i.e. 5 or 8) the percent degradation is decreased (Figure 4f) to minimum because of the non-existence of any attraction from the catalyst. Such type of observation has also been made in a previous study (Palma-Goyes et al., 2014).

3.3. Catalyst recycling experiments

For a practical implementation of heterogeneous catalytic system, it is crucial to evaluate the stability of the catalyst on repeated use. The used catalyst was recovered by filtration, thoroughly washed with water, dried and used again, at optimized condition (100 mg/L dye, 500 mg/L CuO/FAZ catalyst, H\textsubscript{2}O\textsubscript{2} = 5 mL/L, pH = 6.5). Figure 5 shows the performance of used catalyst in five consecutive runs. In first 3 runs, the catalyst exhibited almost 100% activity in IC degradation. Only in 4\textsuperscript{th} and 5\textsuperscript{th} runs the degradation activity is gradually decreased to 81%. All these observations clearly indicate that the catalyst has sustainability in activity. SEM characterization (Section 3.1.3.) reveals that catalyst was chemically stable and the morphology was not affected by its catalytic role in dye degradation.

3.4. Reaction mechanism

Possible mechanism of IC dye degradation is given below on the basis of the formation of hydroxyl radicals via the reaction between the catalyst and H\textsubscript{2}O\textsubscript{2}, and their attack on the dye molecule to generate reactive intermediate species that decay to the oxidation products. The observation of continuation of the degradation process even after the removal of catalyst from the reaction medium is a good evidence for the presence of intermediate (Gemeay et al., 2003).

\[
\begin{align*}
H_2O_2 + [FAZ - Cu(II)] & \rightarrow OH_2^- + H^+ + [FAZ - Cu(I)] \quad \text{(3)} \\
H_2O_2 + [FAZ - Cu(I)] & \rightarrow [FAZ - Cu(I)OH] + OH^- + [FAZ - Cu(II)] \quad \text{(4)} \\
OH^- + dye & \rightarrow \text{Intermediates} \quad \text{(5)} \\
\text{Intermediates} & \rightarrow \text{Oxidation products} + CO_2 \quad \text{(6)}
\end{align*}
\]

Possible evidences for the degradation of IC dye, the various intermediates formed and the degradation pathway were all obtained from the product analysis with LC-MS, UV-vis spectral and COD studies, whose results are discussed in subsequent sections.

Figure 5. Reusability study of CuO/FAZ.

3.5. LC-MS with ESI-mass studies for product analysis

Figure 6 shows LC-MS ESI-mass spectra of sample from wet catalytic oxidation of IC dye after reaction for 180 min. The fresh IC can show a single peak at m/z = 422 corresponding to the M\textsuperscript{+} molecular ion on IC; but this peak was not detected in the spectra indicating that the dye was completely consumed. However, various new peaks appeared showing that the IC dye was destructed and new products were formed. New peaks at m/z = 246, 213, 168 and 136 Da were observed in the mass spectrum, indicative of new smaller organic by-products with aromatic structures. Especially, the peak appearing at 226 Da is assigned to isatin sulphonic acid, a main intermediate product of IC. This is generated after the disruption of C=C bond and formation of ketonic bond via oxidative approaches. Further oxidation of isatin sulfonyl acid with loss of SO\textsubscript{3} gives isatin at m/z = 147 Da, detected in its deprotonated form [1-H]-. The LC-MS analysis confirmed that isatin was one of the first-level degradation products in the catalytic wet peroxide oxidation of IC (Palma-Goyes et al., 2014; Subbulekshmi and Subramanian, Journal of Environment and Biotechnology Research, Vol. 6, No. 2, Pages 228-237, 2017).
Li et al., 2015). The analysis suggests a sequence of oxidation mechanism (Figure 7), in which the hydroxyl radical preferentially attacks the chromophore center of the dye molecule. Finally ring opening of isatin takes place and the intermediates lead to the formation of organic acids (formic acid) converted into CO₂ and H₂O. It is noteworthy that the degradation of IC by both systems (heterogeneous Fenton like catalytic and photocatalytic degradation) leads to the formation of the same set of products (Flox et al., 2006; Costa and Prado, 2009; Palma-Goyes et al., 2014; Li et al., 2015).

3.6. UV-Visible spectral studies

The decrease in the absorbance of IC at λ_max 608 nm during the wet catalytic peroxide oxidative degradation experiment is shown as inset in Figure 6. The decrease in absorbance is due to the loss of conjugation and chromophoric group in IC dye leading to colorless simpler oxidation products. There are no additional peaks appearing in the UV-Vis spectra, confirming that the IC dye is degraded to smaller fragments and finally converted into CO₂ and H₂O.

3.7. Mineralization of IC dye

The reaction intermediates obtained during the oxidation of dyes could be stable and even more toxic than the initial dye; therefore, the decay of intermediate products resulting from the mineralization of dye need to be investigated (Palma-Goyes et al., 2014; Subramanian and Subbulekshmi, 2016). The mineralization of IC was confirmed by COD (Chemical Oxygen Demand) measurements. COD is an important parameter to characterize the organic content of wastewater in aqueous solution. The COD value was determined after degradation of IC dye for 3 h using K₂Cr₂O₇ oxidation method. The COD removal values of the reaction mixture after IC degradation over CuO/FAZ (optimal condition: catalyst = 500 mg/L, 100 mg/L IC and H₂O₂ = 5 mL/L, pH = 6.5) was 80% for 1 h, 91% for 2 h, 100% for 3 h, respectively. From this, it was observed that the solutions obtained after wet catalytic peroxide oxidation showed a significant decrease in COD after 60 and 120 min reaction time. After 180 min, complete mineralization of dye intermediates to CO₂ and H₂O was achieved. LC-MS, UV-Vis and COD results were, thus, in accordance with the degradation
of the dye molecule into smaller fragments and then to CO₂ and H₂O.

4. CONCLUSIONS

The present work demonstrates that fly ash converted and CuO incorporated zeolite, i.e., CuO/FAZ catalyst has high activity and plays a decisive role in the wet catalytic peroxide oxidative degradation of IC dye through efficient production of OH from H₂O₂. This is evident by the result that pure CuO and FAZ have low degradation efficiencies for IC dye when compared to the efficiency of CuO/FAZ. Therefore zeolite and CuO together exhibit synergism in CuO/FAZ catalyst leading to an exceedingly high activity for IC dye decolorisation and mineralization. The dye destruction was confirmed by LC-MS and UV-vis spectroscopy and COD studies. Thus the present work has established that a high degree of Fenton-like activity could be instituted in zeolite from coal fly ash by the introduction and immobilization of CuO secondary catalyst. Applicability of the developed heterogeneous catalyst CuO/FAZ for repeated use was also confirmed by the sustainability of the greater efficiency and the chemical stability of the catalyst even on 5th catalytic run.

REFERENCES


