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Fluidized-bed reactor supported by copper based nanocomposite for oxidative decolourization of recalcitrant dye wastewater

Titikshya Mohapatra, Manisha and Prabir Ghosh*

Department of Chemical Engineering, National Institute of Technology Raipur, Raipur-492 010, Chhattisgarh, India

E-mail: prabirg.che@nitrr.ac.in

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Dye, a colouring compound, is commonly found in various industrial wastewaters like textile, paper and pulp, tannery etc. In this present work, a novel catalyst copper based nanocomposite (Cu-Clay/CS) was synthesized via co-precipitation method in an ultrasonic probe sonicator. Characterization of Cu-Clay/CS was obtained by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and Fourier transform infrared spectroscopy (FTIR). The catalytic activity of prepared catalyst was investigated by Fenton-like oxidation of Eosin Yellow (EY) dye wastewater in a fluidized-bed reactor. The Fenton-like oxidation of dye wastewater was carried out by varied experimental parameters such as pH, oxidant concentration (H_2O_2) and support material dosage to optimize the process efficiency. About 82.3% of the decolourization efficiency was achieved also it showed decrease in the decolourization efficiency with excess of oxidant addition due to scavenging effect. Stability and reusability of catalyst was also studied.

Keywords: Fluidized-bed oxidation, dye wastewater, nanocomposite.

Introduction

Industrial activities are moving towards social and economic development and on the other hand it causes water pollution by producing huge volume of wastewater. Numerous pollutants such as pesticides, dye, surfactants, pharmaceuticals etc. are present in industrial wastewater[1]. Among the pollutants, dye is colouring agent used in many industries e.g. tannery, textile, paper and pulp, food, paint, hair colouring etc. Annual production of synthetic dye is around 10,000 tonnes, about 10% of dyes comes in the wastewater stream from various different industries[2]. The discharge of effluent containing dye is a serious concern for human health and environment because it is toxic, carcinogenic and mutagenic in nature. Discharge of dye effluent to any water body affects the photosynthesis process of aquatic biota as dye has a capability to prohibit the sun light passing into the water body leading to decline the dissolved oxygen (DO) concentration in the water body[3]. It also increases biochemical oxygen demand (BOD) along with chemical oxygen demand (COD) in surface water sources[4]. Hence, there is an urge to treat the dye effluent before its disposal.

Typically biological, physical, chemical methods have been used for the treatment of wastewater containing organic pollutants. Dyes have complex aromatic structure and it has good stability in water. Biological method is inefficient for complete degradation[5]. Physical treatment like adsorption only changes the phase of aqueous organic on to a solid surface without breaking down the contaminant[6,7]. But chemical methods completely degrade the organic contaminants. Among various chemical treatments, advanced oxidation processes (AOPs) are the assuring techniques to get efficient degradation of dye based effluent. Fenton process is getting more attention in AOPs due to its simple handling, cost-effectiveness and pollutant degradation efficiency. Reaction of metal ion with Fenton's reagent hydrogen peroxide (H_2O_2) generates free radicals i.e. hydroxyl radical ($^{\bullet}OH$) shown in eq. (1), it non-selectively reacts with organic pollutants and break down them into innocuous products shown in eq. (3).

$$Fe^{2+} + H_2O_2 \rightarrow {}^{\bullet}OH + Fe^{3+} + OH^- \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (2)$$

$$^{\bullet}OH + \text{Organic pollutants} \rightarrow CO_2 + H_2O \quad (3)$$

Fe^{3+} react with H_2O_2 leads to formation of hydroperoxyl radical ($HO_2^{\bullet}$) and also regeneration of Fe^{2+} ion happens, termed as Fenton-like process shown in eq. (2). Though $HO_2^{\bullet}$ radical is a weaker oxidant than $^{\bullet}OH$ radical[8], but it has contribution in the degradation of organic contaminants. Huge amount of sludge production is the main flaw of the Fenton process which demands further treatment and dumping. To beat this matter, Fenton process can be coupled with the fluidized-bed reactor. In a fluidized-bed Fenton process, the reactor contains solid carrier material which behaves like a fluid by passing fluid (liquid/gas) through it, provides a surface for the precipitation as well as the crystallization of iron sludge upon it. Thus, sludge formation can be reduced in this process.

Metals except iron having more than one oxidation states e.g. Cu, Cr, Al, Mn etc. have ability to form hydroxyl radical ($^{\bullet}OH$) by decomposition of H_2O_2[9]. The objective of the study is synthesis of heterogeneous Fenton-like catalyst like copper based nanocomposite (Cu-Clay/CS). Eosin Yellow (EY) was chosen as a model pollutant, which is a disodium salt based dye having red fluorescent colour used in ink manufacturing, textile and cosmetic industries[10,11]. Degradation of EY dye wastewater was carried out by fluidized-bed oxidation process with the support of prepared catalyst and process performance was evaluated by varying pH, H_2O_2 concentration and carrier material dosage.

Material and method

EY dye used as a model pollutant, H_2O_2 was used as oxidizing agent (30% w/v). Copper sulfate ($CuSO_4.5H_2O$) (98.5% purity), bentonite powder, sodium borohydride ($NaBH_4$) (98% pure) and chitosan were employed for the synthesis of catalyst. To maintain the pH of the solutions, H_2SO_4 and NaOH were used.

Synthesis of the catalyst:

The Cu-Clay/CS catalyst was prepared by supporting copper nanoparticles on the bentonite clay and formation of catalyst beads was done using chitosan. Firstly, 0.04 *M* copper sulfate solution was prepared using deionized water and 5% (5 g/100 ml) bentonite clay (Clay) was added to form the mixture. Then, it was stirred for 1 h using a magnetic stirrer. 0.13 *M* $NaBH_4$ was added to the copper-bentonite solution in 1:1 ratio. Sodium borohydride was used as a reducing agent. The mixture was transferred into a round bottom high neck flask assembled with probe ultrasonicator for making the mixture homogeneous. It was observed that the color of the solution changes. At this stage, the mixture was further irradiated under ultrasonicator for 45 min. The suspension was then centrifuged at 3000 rpm for 10 min. After centrifugation, the supernatant was removed and the precipitate was washed thoroughly with deionized water and ethanol to remove impurities. The precipitate was then dried at 50°C in a hot-air oven for 2 h. 2 g of chitosan (CS) was mixed with 1% v/v 100 ml acetic acid solution and it was stirred continuously at 50–60°C until the chitosan dissolved completely. Then dried Cu-Clay was added into the chitosan solution and mixed till the solution becomes homogenous. Drop wise addition of this homogenous mixture into NaOH solution instantly formed beads as shown in Fig. 1. The beads were strained and washed thoroughly with the deionized water and dried at room temperature.

Analysis and characterization techniques:

The morphology of the synthesized nanocomposite was observed by scanning electron microscopy (SEM) and the elemental composition of the nanocomposite was analyzed by energy-dispersive X-ray spectroscopy (EDX). Using Fourier transform infrared spectrophotometer (FTIR), the functional groups on the catalyst surface were obtained. Dye concentration was measured by UV-Vis spectrophotometer (Shimadzu, UV-1800, Japan) at 517 nm.

$$\text{Degradation efficiency} = \frac{C_i - C_t}{C_i} \times 100 \quad (4)$$

where C_i and C_t are the dye concentration of wastewater at t = 0 and after time t, respectively.

Experimental procedure:

The experiments were carried out in the cylindrical fluidized-bed with the length 0.22 m, ID of 0.028 m and a thickness of 0.003 m. The catalyst and inert carrier (silica beads) were fluidized by an air pump with air flow rate ranging from

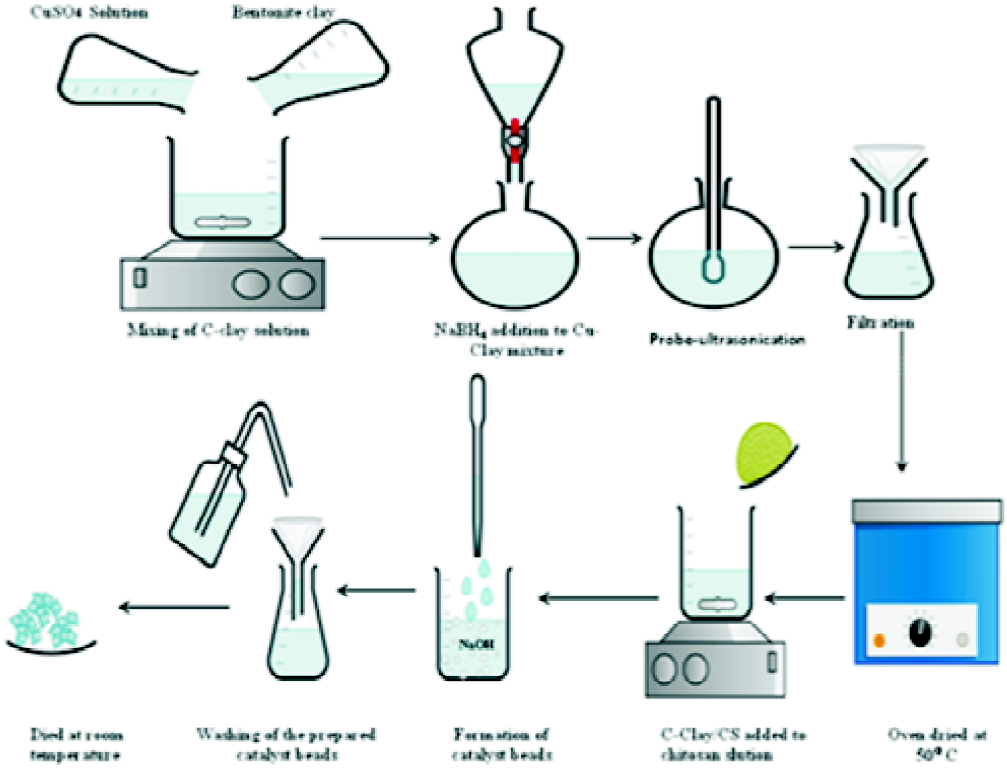

Fig. 1. Synthesis of catalyst.

0–3.5 L/min. In this study, a synthetic wastewater of EY was prepared with concentration of 100 mg/L. pH was adjusted. This was followed by addition of H_2O_2 to initiate the Fenton reaction. The air was passed through the bottom of the reactor (shown in Fig. 2) to initiate the fluidization. Samples were collected at equal intervals from the outlet of the reactor and were analyzed.

Results and discussion

Characterization of Cu-Clay/CS:

SEM was used to investigate the surface morphology of prepared Cu-Clay/CS nanocomposite. Fig. 3 represents the SEM image of Cu-Clay/CS, it was observed that the particles are irregular and coarse. The elemental composition of the catalyst was determined using EDX. It indicates the existence of iron, copper, silica and aluminum in the prepared nanocomposite shown in Fig. 4. To know about the functional groups present in the catalyst, FTIR analysis was performed using Bruker, Alpha model in a wide range 4000–500 cm^{-1}. The Fig. 5 presents the FTIR spectra of Cu-Clay/CS and Table 1 shows the FTIR analysis of the catalyst. The XRD patterns are analysed using PANalytical 3 kW X'pert powder X-Ray diffractometer with a Cu Kα radiation source in 2θ range of 5–80°. The crystalline phase, crystalline size, crystalline purity of the prepared catalyst was determined using XRD. X-Ray diffraction was used to ascertain the crystallography of the catalyst. Fig. 6 shows a graph between intensity vs 2θ. It is evident that the catalyst is highly crystalline in nature.

Effect of nanocomposite dose on EY degradation in a fluidized-bed oxidation process:

The nanocomposite provides surface to oxidizing agent H_2O_2 to react with it and produce hydroxyl radicals (•OH). Fig. 7 displays the effect of nanocomposite dosage on the degradation of EY. Cu-Clay/CS dosage variation was done from 0.1 to 0.5 g at constant pH 5 and H_2O_2 concentration 20 mM. The EY degradation efficiency increased with the increase in catalyst dosage till 0.4 g, after that further increase in nanocomposite dosage drives to decline the deg-

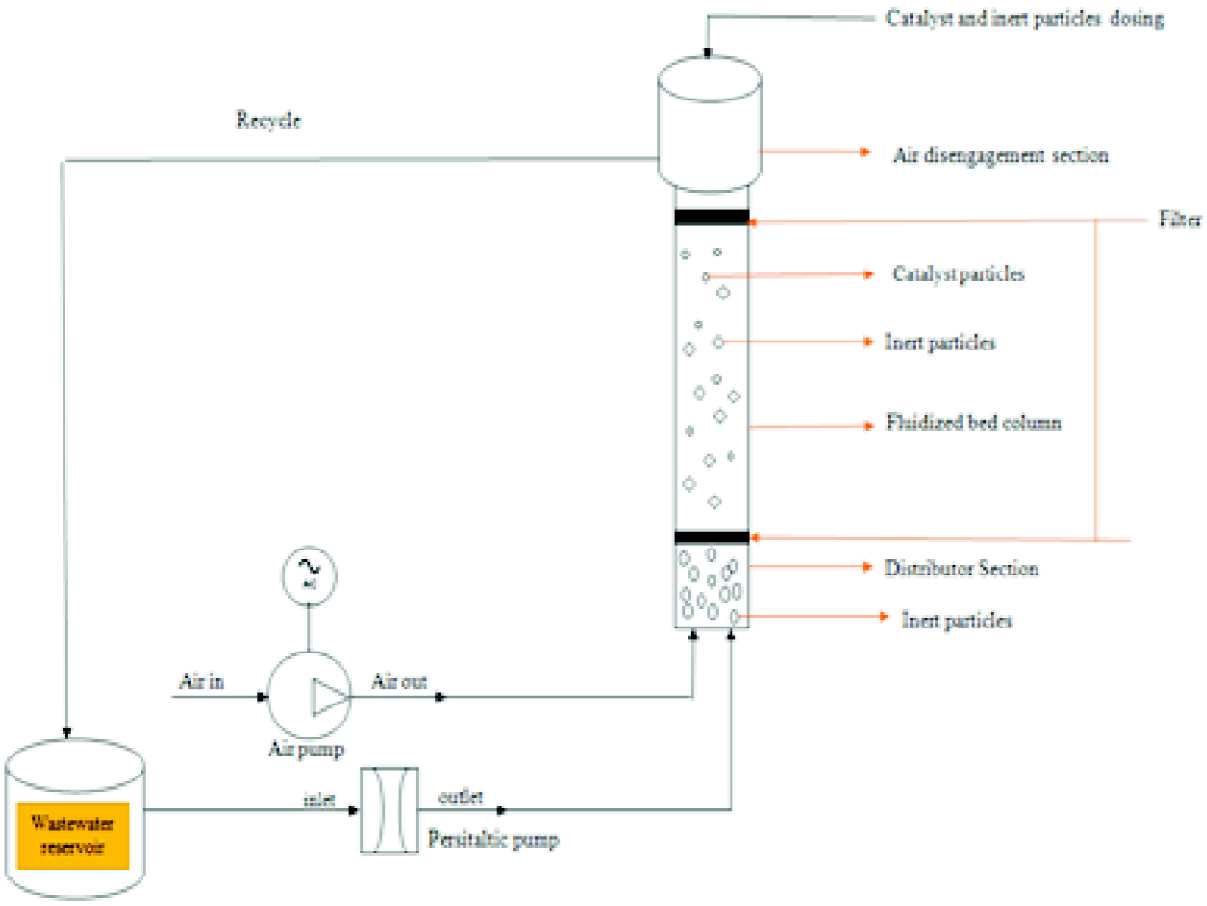

Fig. 2. Experimental set-up.

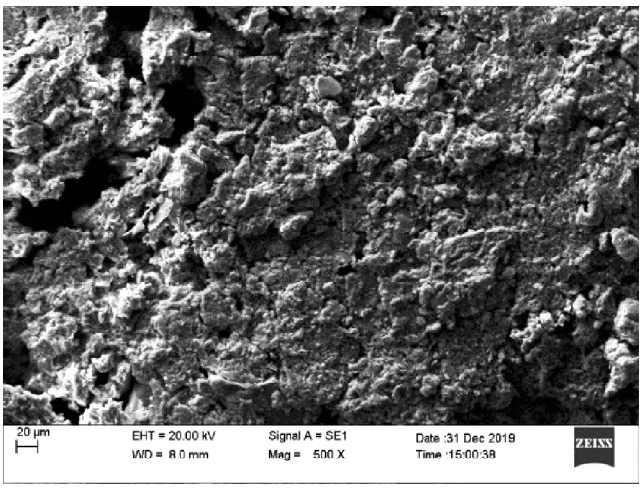

Fig. 3. SEM image of Cu-Clay/CS.

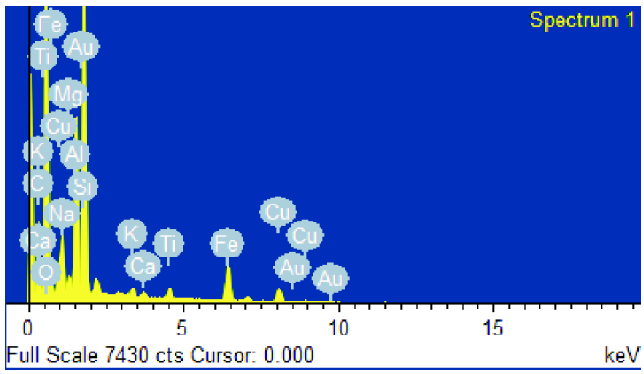

Fig. 4. EDX analysis of Cu-Clay/CS.

radation efficiency. It may be due to more load of catalyst which scavenges •OH radicals as represented in eq. (5)[12].

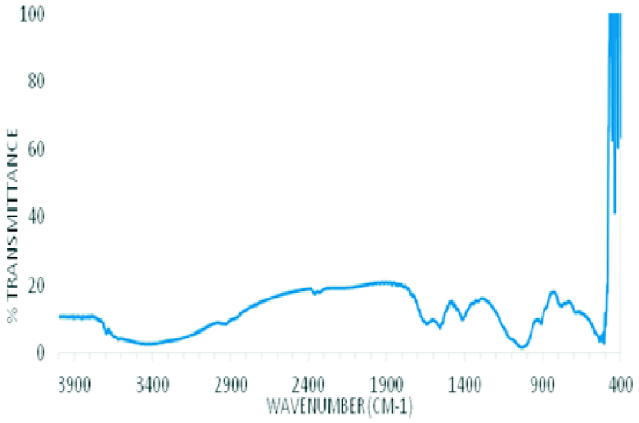

Fig. 5. FTIR spectrome of catalyst.

Table 1. FTIR group characterization

Bond	Wave-number
O-H stretching	3706
N-H stretching	3643
C=C stretching	1666
Si-O-Si stretching, -OH and -NH_2 with Cu^{2+}	1061
Si-O-Si bending	802
Bending between metal and oxygen	543

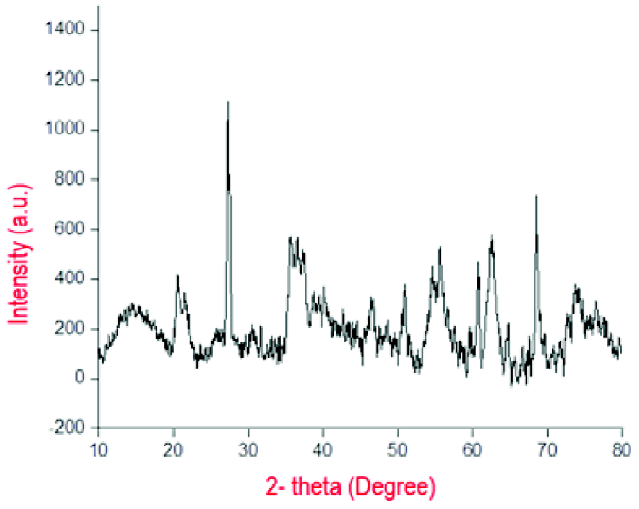

Fig. 6. XRD profile of catalyst.

$$Fe^{2+} + {}^{\bullet}OH \rightarrow OH^{-} + Fe^{3+} \quad (5)$$

Effect of pH on EY degradation in a fluidized-bed oxidation process:

In the Fenton process, pH also plays a significant role.

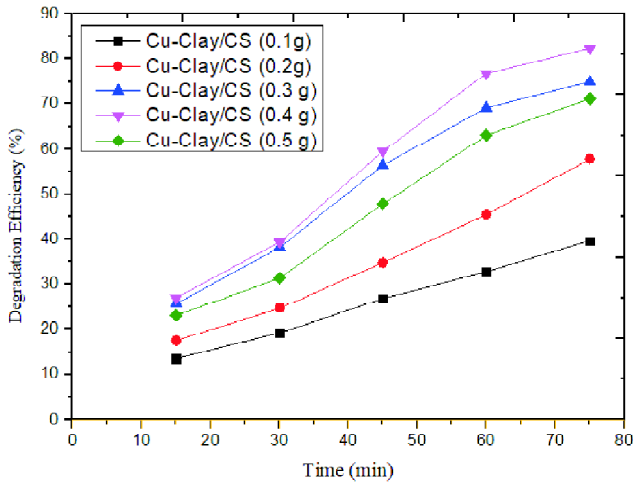

Fig. 7. Effect of catalyst dosage initial EY = 100 mg/L, H_2O_2 = 20 mM, Q_{air} = 0–3.5 L/min, pH = 5.

To determine the optimum pH in fluidized-bed Fenton process, pH was varied from 4 to 7. The EY degradation concerning pH is shown in Fig. 8. The better decolorization was achieved by maintaing the pH at 5, retaining H_2O_2 and Cu-Clay/CS dosage at 20 mM and 0.4 g, respectively. It was observed that EY degradation efficiency was decreased with successive increment in pH. This is due to the formation of •OH radical becomes lesser at higher pH. Also the efficiency of EY degradation was low at lower pH as the regeneration of ferrous iron from ferric iron is very slow at very acidic medium[13].

Effect of H_2O_2 on the degradation efficiency in fluidized-bed oxidation process:

Oxidant is the main object of Fenton process. The pro-

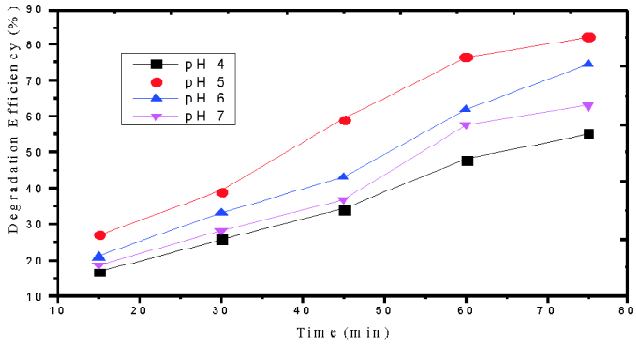

Fig. 8. Effect of pH at initial EY = 100 mg/L, H_2O_2 = 20 mM, Q_{air} = 0–3.5 L/min, Cu-Clay/CS = 0.4 g.

cess cost depends on the requirement of H_2O_2, thus it needs to be optimized in fluidized-bed Fenton process. The degradation of EY was examined by varying H_2O_2 from 10 mM to 25 mM keeping the pH and nanocomposite dosage at 5 and 0.4 g, respectively. Fig. 9 shows the degradation efficiency was increased with the increase in H_2O_2 concentration till 20 mM, further increase in oxidant concentration shows a decline in the degradation efficiency. This is because excess of H_2O_2 concentration produce hydroperoxyl radical ($^{\bullet}O_2H$) by scavenging hydroxyl radical ($^{\bullet}OH$) shown in eq. (6)[4,12].

$$H_2O_2 + {}^{\bullet}OH \rightarrow {}^{\bullet}O_2H + H_2O \quad (6)$$

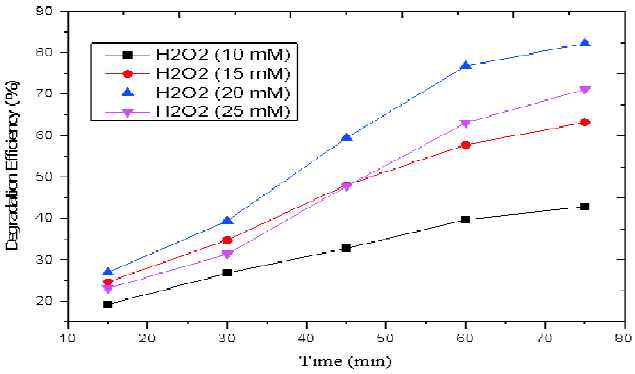

Fig. 9. Effect of H_2O_2 dosage at initial EY = 100 mg/L, Cu-Clay/CS = 0.4 g, Q_{air} = 0–3.5 L/min, pH = 5.

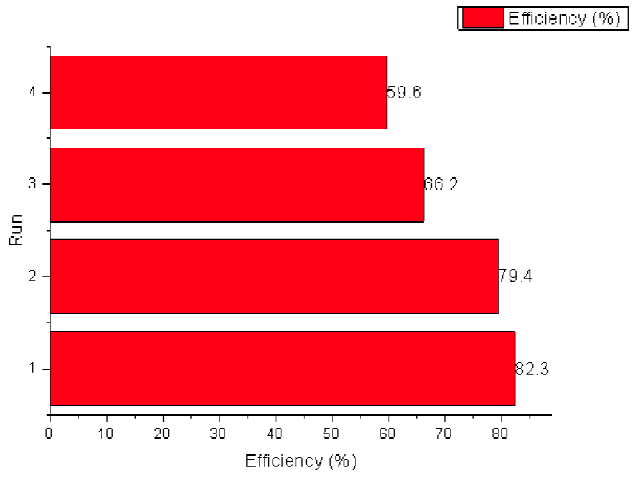

Fig. 10. Catalyst reusability for 4 runs at initial EY = 100 mg/L, H_2O_2 = 20 mM, pH = 5, Cu-Clay/CS = 0.4 g, Q_{air}=0–3.5 L/min.

Catalyst reusability:

In this study, reusability of the prepared nanocomposite was examined for 4 runs. The catalyst was washed after each run and dried at room temperature and was used in treatment of the synthetic wastewater at optimum conditions. It was observed that after each run the efficiency slightly got decreased shown in Fig. 10.

Conclusions

The main purpose of this study is to address the wastewater treatment using nanocomposite particles in a fluidized-bed Fenton-like process. Various operating variables affecting the Fenton-like process were investigated in this study for the degradation of synthetic dye wastewater (EY dye). It was found that the prepared Cu-Clay/CS nanocomposite catalyst has the potential to degrade the model pollutant in this system. The optimum conditions were determined as [Cu-Clay/CS]: 0.4 g, [H_2O_2]: 20 Mm and pH 5. The degradation efficiency was observed to be 82.3% within 75 min of reaction time. The following study shows the reusability of the catalyst up to four runs even though the efficiency slightly decreased in each run.

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