Oxidative degradation of Congo red using zeolite Y as a support for Co(II), Ni(II) and Cu(II) ions

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Abstract

In this paper, the potential of Co(II), Ni(II) and Cu(II) incorporated zeolite Y prepared via wet impregnation process, was studied in Catalytic wet air oxidation of Congo red. The catalysts were characterized with AAS, FTIR, XRD, SEM, BET Surface area and cation exchange capacity measurement. The results revealed that all the three incorporated zeolite Y catalysts showed significant loss of crystallinity due to the heavy loading of respective metal ions. The dye was decolourised to the extent of 95.90, 97.54 and 87.79% by Co(II)–zeolite Y, Ni(II)–zeolite Y and Cu(II)–zeolite Y respectively in 4 h at a solution pH of 6.4, catalyst load of 1.5 g L^{-1} , initial dye concentration of 10.0 mg L^{-1} and temperature 303 K. All the reactions followed second order kinetics with good linearity (Regression coefficient $R = 0.95\text{--}0.97$). The overall chemical oxygen demand reduction of the dye with Co(II)–zeolite Y, Ni(II)–zeolite Y and Cu(II)–zeolite Y were 95.51, 98.62 and 90.70% respectively, confirmed the mineralization of the dye. Thus these incorporated catalysts could be considered as promising catalysts for the degradation of Congo red and they can be recovered and reused up to three consecutive runs effectively.

Keywords Zeolite Y · CWAQ · Crystal violet · COD

1 Introduction

Textile industries generated a huge amount of coloured wastewater containing wide variety of dyes in different concentration. During the textile production processes, 10–15% of the total dye remains untreated and the residual dyestuffs are discharged as effluent [1]. These effluents from dye house are characterised with intense colour, broad range of pH, high chemical oxygen demand (COD) and total dissolved solids (TDS) and low biodegradability, causing a serious environmental concern [2, 3]. Among different dyes, Congo red (CR) an anionic diazo dye has been widely used in textile, rubber, paper and plastic industries [4, 5]. In spite of its various use, the dye is known to possess carcinogenicity and may also lead to tumor formation amongst humans. Accumulation of this dye can cause irritation of the eye and skin, vomiting and diarrhoea. In fact the use of Congo red has been banned in many countries [6]. Therefore, it is necessary to remove the problematic

substance from wastewater before discharged into surface water. Various biological and physico-chemical techniques have been employed to remove colour from wastewater [7–14]. However, all these processes have some significant disadvantages like high sludge production, high energy requirement, cause some secondary pollution problems by transferring the dye molecules from one phase to another and thereby making the processes not economically feasible.

Recently, advanced oxidation process (AOP) has received great attention among researchers as a technique for the treatment of wastewater containing textile dyes with great degree of success. AOP with the generation of strong and non-selective oxidising agent such as hydroxyl radical is the most effective and economic way to degrade the organic pollutants [15]. Common AOPs include Fenton, photo-Fenton, wet oxidation, ozonation, electrochemical oxidation, photocatalysis and combination of these methods [16–22]. Among this wet air oxidation (WAO), which

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was proposed by Zimmermann [23] has great potential to treat refractory organic pollutants at elevated temperature (175–320 °C) and high pressure (0.5–20 MPa) using pure oxygen or air as oxidant. Use of proper catalysts for WAO known as catalytic wet air oxidation (CWAO) relax the oxidation process and reduce capital and operational cost [24, 25]. Although homogenous catalysts are effective for CWAO, requirement of additional separation step to remove catalyst ions from the treated effluents limit its applications [26]. Thus the development of an effective heterogeneous catalyst has received great attention. Various heterogeneous catalysts such as metal oxides, noble metals, mixed oxides and supported metal catalysts on porous solid materials have been prepared and studied for CWAO to treat different organic pollutants in

wastewater [27–30]. In particular, zeolites modified with transition metal ions have been reported as promising solid catalyst to remove organics from wastewater [31, 32]. The improved efficiency of zeolite as a support is due to its channels and cage like structure and high surface area that allow the adsorption of large organic molecules on its surface as well as less by-product formation make the process eco-friendly. The structure of zeolite Y zeolite Y is shown in Fig. 1. Again transition metal ions with the ability of change in their oxidation state undergo various redox reactions occurring in the environmental processes. In our previous work we have used Cu(II)–zeolite Y as a catalyst for the oxidation of both cationic and anionic dyes [33].

In the present work, zeolite Y was incorporated with Co(II), Ni(II) and Cu(II) ions via wet impregnation and were used as catalyst for the oxidation of Congo red dye in aqueous medium. In order to evaluate the optimum operating conditions the oxidation processes were carried out with process variable such as pH, temperature, amount of catalyst, dye concentration and interaction time. The importance of the work lies in the fact that simple wet impregnation process was used for incorporating metal ions into the zeolite surface and the oxidation process did not required any external oxidising agent thereby making the process cost effective and eco-friendly.

Fig. 1 Structure of zeolite Y

2 Materials and methods

2.1 Chemicals

Here, Congo red (CR) dye was used as a model pollutant for studying the oxidative degradation process. Few important properties of the dye were given in the Table 1. Incorporation of the respective metal on zeolite Y was done by using Co(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Ni(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and Cu(II) Nitrate

Table 1 Properties of Congo red dye

Properties	
Molecular formula	$\text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2$
IUPAC name	1-napthalene sulphonate, 3,3'-(4,4'-biphenylenebis(azo) bis(4-amino-) disodium salt]
Chemical structure	
Molecular weight (g mol^{-1})	696.66
Maximum wavelength (nm)	498.00 (in aqueous solution)
Melting point	360 °C

trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$). All these Chemicals were purchased from E. Merck, Mumbai, India. Pure Zeolite Na–Y was purchased from Himedia Laboratory Private, India. All other Chemicals used here were of analytical grade and distilled water was used throughout the experiment.

2.2 Preparation of metal incorporated catalyst

The metal-incorporated catalysts were prepared by refluxing 25 g Zeolite Na–Y separately with 100 mL of 1.0 M solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ for 6 h in a 500 mL round-bottom flask at room temperature. The sample was filtered, washed repeatedly with distilled water several times and then dried in a hot air oven. Each of them was calcined for 2 h at 773 K in a muffle furnace and was preserved. Altogether four catalysts were obtained and we named zeolite Y, Co(II)–zeolite Y, Ni(II)–zeolite Y and Cu(II) zeolite Y as Y, Y1, Y2 and Y3 respectively.

2.3 Preparation of stock solution

A stock solution of Congo red having concentration 1000 mg L^{-1} was prepared. All the dye solutions required for the experiments were made from the stock solution in different concentration by diluting with distilled water.

2.4 Characterization of the catalyst

The structural features of the prepared samples were identified by Fourier Transform Infrared spectroscopy (FT-IR) measurement (Shimadzu FT-IR 3000 Spectrometer, range $400\text{--}4000 \text{ cm}^{-1}$) using KBr self-supported pellet technique. The phase structure and the phase composition of the samples were done by X-ray powder diffraction (XRD) measurement (Philips analytical X-Ray Spectrophotometer, PW 1710, Cu K α radiation, CuK α radiation source at the 2θ range of $5\text{--}80^\circ$). The surface morphology and the elemental composition of the samples were determined with a scanning electron microscope (SEM) measurement (JEOL JSW-6360). The specific surface area and pore volume of the prepared samples were calculated using Brunauer–Emmett–Teller (BET) and Barret–Joyner–Halender (BJH) method (Micromeritics Tristar surface area and porosity analyzer). The amount of Co(II), Ni(II) and Cu(II) entering into the zeolite Y were determined by atomic absorption spectrophotometry (AAS) measurement (Perkin Elmer AAnalyst 220) and cation exchange capacity (CEC) of the prepared samples were determined by using Copper bisethelenediamine complex method.

2.5 Experimental procedure for wet oxidation of the dye

The catalytic oxidation was carried out in a water bath shaker (NSW, New Delhi, India) by agitating 20 mL of Congo red in 50 mL Erlenmeyer flasks with a catalyst load each of 1.5 g L^{-1} . After the completion of the reaction, the mixture was centrifuged (Remi Research Centrifuge, R 24) to remove the solid catalyst and the remaining unconverted dye was estimated spectrophotometrically (Shimadzu 1800 UV–Vis spectrometer) at a λ_{max} of 498 nm. The batch experiments were carried out under different experimental conditions as shown in Table 2. To study the effect of pH on the oxidation process pH of the reaction mixture was measured by digital pH meter and the same was adjusted by adding few drops of 0.1 N HNO_3 or 0.1 N NaOH solutions. All the experiments were repeated three times to avoid the experimental error.

2.6 Monitoring chemical oxygen demand

Reduction of Chemical oxygen demand (COD) of the reaction mixture was determined by open reflux method [34]. In this method, 10 mL of dye solution was mixed with 20 mL 0.0417 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution, 30 mL conc. H_2SO_4 and a pinch of silver sulphate along with glass beads. The mixture was refluxed for 2 h and then cooled. 80 mL distilled water was added to the reaction mixture and was titrated with 0.25 M Ferrous ammonium sulphate (FAS) solution using ferroin as indicator to determined the amount of unreacted $\text{Cr}_2\text{O}_7^{2-}$. The whole procedure is first done with 10 mL of distilled water in place of dye solution.

2.7 Measurement of conversion

The conversion of dye was calculated from the decrease in concentration of the dye and the percentage conversion of the dye was expressed as

$$\% \text{ conversion} = [(C_i - C_f)/C_i] \times 100 \% \quad (1)$$

where C_i and C_f are the initial and final concentration (mg L^{-1}) of the dye respectively.

Table 2 Experimental conditions for wet air oxidation of Congo red

Sl. no.	Process variable	Variation range
1	Volume of reactant	20.0 mL
2	Reactant concentration	1.0, 10.0, 50.0 and 100 mg L^{-1}
3	Catalyst loading	0.5, 1.0, 1.5, 2.0 g L^{-1}
4	pH	4.0, 6.0, 8.0, 10.0
5	Temperature	303–343 K
6	Pressure	Atmospheric pressure
7	Reaction time	5–300 min

Chemical oxygen demand (COD) of the reaction mixture was estimated by using the standard open reflux method (APHA, 1989) and COD removal percentage was calculated as

$$\% \text{ COD removal} = \left[(\text{COD}_o - \text{COD}_t) / \text{COD}_o \right] \times 100\% \quad (2)$$

where COD_o and COD_t are COD of the dye (mg L^{-1}) before and after oxidation respectively.

3 Results and discussion

3.1 Characterization of the catalysts

3.1.1 AAS measurement

The amount of Co(II), Ni(II) and Cu(II) entering into zeolite Y was determined with atomic absorption spectroscopic (AAS) measurement. The incorporation of transition metal ions into the zeolite Y materials considerably increased the metal ion concentration. The raw zeolite Y contained 0.315 mg kg^{-1} Co(II) and on incorporation, amount of Co(II) increased to $36.247315 \text{ mg kg}^{-1}$. When incorporated with Ni(II), the content increased from 0.213315 (in raw zeolite) to $18.395315 \text{ mg kg}^{-1}$ and with Cu(II), the same was increased from 0.037315 to $17.061315 \text{ mg kg}^{-1}$. Thus the content of metal ion after incorporation in zeolite Y are in the order of: Co(II) > Ni(II) > Cu(II).

3.1.2 Cation exchange capacity

The presence of metal ion species was further checked with cation exchange capacity (CEC) measurement. The metal incorporation enhanced the CEC value of zeolite Y to 11.02 (Y1), 10.84 (Y2) and 10.25 (Y3) $\text{meq } 100 \text{ g}^{-1}$ (CEC increase $\sim 13\%$ in Y1, $\sim 12\%$ in Y2 and $\sim 7\%$ in Y3). Chaliha and Bhattacharyya [35] reported that CEC of the material increases with increase in the number of cation exchange sites. In the present case, metal incorporation processes increase the number of such exchangeable sites in all the catalysts. According to Rodrigues [36], the ion exchange capacity of the materials occurs due to structural defects, broken bonds on the surface and hydroxyl ion transfer.

3.1.3 FT-IR analysis

FTIR spectra of Co(II)-zeolite Y (Y1), Ni(II)-zeolite Y (Y2) and Cu(II)-zeolite Y (Y3) along with raw zeolite Y are shown in Fig. 2. The observed frequencies of raw Zeolite Y at 450 , 558 , 708 , 1004 , 1432 , 1635 and 3432 cm^{-1} are in good agreement with the data of the previous literature [37]. The absorption band of Y at 1004 cm^{-1} which was assigned

Fig. 2 FT-IR bands of Y, Y1, Y2 and Y3 catalyst

to asymmetric stretching vibration of Si-OAl in tetrahedra, shifted to 1103 cm^{-1} , 1020 cm^{-1} and 1087 cm^{-1} for Y1, Y2 and Y3 respectively. Similar shift of this band from 1018 to 1043 cm^{-1} was observed by Singh et al. [32] where they had reported that this shift was due to the partial dealumination of zeolite framework. They further reported that the small change in the double ring vibration band, observed at 577 cm^{-1} signified small dealumination because of incorporation of metal and calcination. In the present case also, the double ring vibration band in zeolite Y at 558 cm^{-1} was shifted to 603 cm^{-1} , 610 cm^{-1} and 611 cm^{-1} for Y1, Y2 and Y3 respectively. Thus it signifies the incorporation of respective metal with the external linkage of tetrahedral. The Si-O-Si bending vibration at around 450 cm^{-1} , observed in zeolite Y, was present in all the three incorporated catalysts with a very small shift in wavelength and decrease in peak intensity. The OH- stretching and bending vibration in raw zeolite Y were observed at 3432 cm^{-1} and 1635 cm^{-1} respectively. It was found that the broad OH- stretching band was appeared at 3402 cm^{-1} in Y1, 3410 cm^{-1} in Y2 and 3417 cm^{-1} in Y3. At the same time, the OH- bending vibration was observed at 1617 cm^{-1} , 1624 cm^{-1} and 1625 cm^{-1} for Y1, Y2 and Y3 respectively.

3.1.4 XRD analysis

The XRD pattern of zeolite Y and all the metal incorporated zeolite Y catalysts are given in Fig. 3a-d. As shown in Fig. 3a, the characteristic peaks of zeolite Y at 2θ values of 6.3 , 10.3 , 12.1 , 15.9 , 20.7 , 24.0 , 27.5 and 31.9 corresponds to (111), (220), (311), (331), (440), (533), (642) and (555) respectively which are agreed well with the previous studies of Hriljac et al. [38].

XRD patterns show that after the incorporation of Co(II) into zeolite Y (Y1), the crystalline structure of zeolite Y changed significantly (Fig. 3b). Here, the complete diminishing of zeolite Y peaks indicates the high metal loading

Fig. 3 XRD images of raw **a** Y, **b** Y1, **c** Y2 and **d** Y3 catalyst

on zeolite surface. Similar results were obtained by Kondro et al. [39] showing that high loading of transition metal considerably affected the crystallinity of the support.

In case of Ni(II) incorporated zeolite Y (Y2), the characteristic peaks of zeolite Y vanishes and new XRD bands at 2θ of 37.5, 43.6 and 62.2 corresponds to NiO crystallites appears (Fig. 3c). Srivastava et al. [40] have been reported that the peaks at 2θ of 37.1, 43.1 and 62.6 corresponds to the diffracting planes [111], [200] and [220] of cubic NiO crystallites [JCPDS card 47-1049].

Due to the presence of Cu(II) after incorporation, the peaks of zeolite Y diminished along with the evaluation of new peaks (Fig. 3d). The XRD patterns of Cu(II)–zeolite Y show two high intensity peaks at 2θ values 35.5 and 38.7 which could be indexed to (11-1) and (111) reflection of monoclinic CuO crystallite (PDF Files 48-1548). The presence of high intensity peaks proved the presence of

considerable Cu(II) particles inside the pore of zeolite Y [41].

3.1.5 SEM analysis

SEM micrographs of unloaded zeolite Y showed hexagonal shaped crystallites with smooth surface (Fig. 4.Y). When zeolite Y is incorporated with Co(II), the damages in the topography are distinctly visible. It appears that in Y1 the surface of the particles become fluffy with no particular shape as shown in Fig. 4.Y1. In Ni(II)–zeolite Y, the zeolite particles seem to have been less affected after incorporation. Here, (Fig. 4.Y2) the zeolite particles maintain their shapes but crystal size was not uniform and there are some agglomeration observed on zeolite surface which may be ascribed to Ni(II) deposits in zeolite Y. In comparison to the parent zeolite Y, the incorporation of Co(II) and Ni(II) into it

Fig. 4 SEM images of raw and modified Y Zeolite (Y, Y1, Y2 and Y3)

appeared to have changed the zeolite surface. Thus incorporation has exposed new surface sites which might be served for the increased in CEC value as observed earlier. Similar observations have been made by Das and Bhattacharyya [42] after the acid treatment on different metal oxides.

In case of Cu(II)–zeolite Y, we have not observed any major change in their morphologies except a little loss of uniformity in the crystal size distribution after Cu(II) incorporation (Fig. 4.Y3). This observation suggested that Cu(II) ion might be located inside the pores of zeolite Y. Similar results were obtained by Chen and Sun [43] showing that due to the porous structure of zeolite Y, its available surface area was fully occupied by incorporated metal ions. As a result, these metal ions were invisible on the surface of zeolite Y.

3.1.6 BET surface area measurement

All zeolite catalysts in the present work followed typical reversible type IV hysteresis according to IUPAC

convention [44]. The BET isotherms for all the zeolite based catalysts are shown in Fig. 5. Zeolite Y used, here, had a surface area of $485 \text{ m}^2 \text{ g}^{-1}$, which was found to change significantly after metal incorporation. The BET surface area and pore measurements are given in Table 3. It is observed that the BET surface area of zeolite Y was $485 \text{ m}^2 \text{ g}^{-1}$ that decreased to $165 \text{ m}^2 \text{ g}^{-1}$ for Y1, $227 \text{ m}^2 \text{ g}^{-1}$ for Y2 and $287 \text{ m}^2 \text{ g}^{-1}$ for Y3. The pore volume of parent zeolite Y ($0.26 \text{ cm}^3 \text{ g}^{-1}$) decreased to $0.12 \text{ cm}^3 \text{ g}^{-1}$ (Y1), $0.21 \text{ cm}^3 \text{ g}^{-1}$ (Y2) and $0.24 \text{ cm}^3 \text{ g}^{-1}$ (Y3) indicating that Co(II)–zeolite Y has minimum pore volume. In the meantime, the pore size of zeolite Y ($8.35 \text{ \AA}$) decreased to $5.73 \text{ \AA}$, $7.24 \text{ \AA}$ and $7.45 \text{ \AA}$ in Y1, Y2 and Y3 respectively.

Substantial decrease in surface area, pore volume and pore size of all the metal incorporated catalysts observed in the present case might be due to the deposition of respective metal species into pores and/or the external surface of support material. The deposition of particular metal ion on the external surface leads to agglomeration and formation of metal oxide as supported by XRD studies. This large decrease in surface area as well as pore

Fig. 5 BET adsorption–desorption isotherms of **a** Y, **b** Y1, **c** Y2 and **d** Y3

Table 3 Surface and pore characteristics of zeolite and its metal incorporated form

Materials	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
Y	185	0.26	8.35
Y1	165	0.12	5.73
Y2	227	0.21	7.24
Y3	287	0.24	7.45

volume after incorporation is consistent with the loss of crystallinity of zeolite [45]. Rache et al. [46] found similar large decrease in surface area from 432 to 259 m² g⁻¹ and pore volume from 0.24 to 0.10 cm³ g⁻¹ of zeolite Y when exchange with Fe ion for the degradation of Orange II dye.

Aravindhan et al. [47] reported that decrease in surface area of doped zeolite Y was due to the incorporation of high concentration of metal ion inside the zeolite surface. However, a different result was obtained by Kondru et al. [39] as the BET surface area of zeolite Y slightly decreased from 433 to 423 m² g⁻¹ after doping with Fe ion. They recommended that small decrease in surface area after doping was due to the low loading of metal ion and its insertion did not produce any significant affect to the support. Again the reduction of the pore measurements after incorporation into zeolite surface could be attributed to the blocking of pore opening as obtained by Hajimizaee et al. [48]. Based on the above facts it can be concluded that, in the present work, high concentration of metal ions [Co(II), Ni(II) and Cu(II)] were successfully incorporated inside zeolite Y.

3.2 Wet air oxidation of methylene blue

3.2.1 Blank experiment

Before investigating the catalytic oxidation process, blank experiments were carried out to observe self-decolorization of the dye. No measurable conversion was observed when 20 mL of an aqueous solution of Congo red was agitated under the same conditions as were used for the metal incorporated zeolite Y catalysts.

3.2.2 Effect of reaction time and kinetics

In all the cases, the reactions reached near equilibrium conditions after 240 min (Fig. 6). In the time interval of 5–300 min, the increase in conversion was: 7.44–26.38% for Y, 56.97–95.90% for Y1, 60.28–97.54% for Y2 and 47.22–87.79% for Y3. In each case, the oxidative reactions were carried out with catalyst load of 1.5 g L^{-1} , dye concentration of 10.0 mg L^{-1} at 303 K and 1 atmospheric pressure. Kundru et al. [39] reported that 99.1% congo red removal could be obtained by catalytic wet peroxide oxidation at 100 °C in 4 h using 0.6 mL H_2O_2 /350 mL solution and 1 g Fe–zeolite Y catalyst. In the present work, maximum 97.54% decolorization of CR was achieved in absence of H_2O_2 and at 30 °C using $1.5 \text{ g Ni(II)-zeolite Y (Y1)}$ catalyst.

The oxidative reactions were found to follow the second order kinetics according to the following rate equation

$$dC/dt = k(C_0 - C_t)^2 \quad (3)$$

$$\text{or } 1/C_t = kt + 1/C_0 \quad (4)$$

where C_0 and C_t are initial and concentration at any time (t) respectively and k is the second order rate constant. The plots of $1/C_t$ versus time were linear (regression coefficient,

$R = 0.95\text{--}0.97$) as shown in Fig. 7. Singh et al. [31] had shown that degradation of Congo red with Cu impregnated Zeolite Y followed first order kinetics. In the present work first order kinetics were also tested but deviated much from linearity. The second order rate coefficients obtained from the plots are given below:

$$Y : 1.78 \times 10^{-4} \text{ g mg}^{-1} \text{ min}^{-1}$$

$$Y1 : 6.31 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$$

$$Y2 : 9.32 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$$

$$Y3 : 1.76 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$$

Thus the second order rate coefficients follow the order $Y2 > Y1 > Y3 > Y$ indicating that Ni(II)–zeolite Y has a higher rate of conversion of CR in aqueous solution.

3.2.3 Effect of catalyst load

Oxidation of Congo red (100.0 mg L^{-1}) at 303 K and atmospheric pressure increased gradually with increase in zeolite Y catalyst load. When the catalyst load was increased from 0.5 to 2.0 g L^{-1} , the CR oxidation increased from 16.50 to 25.57% for Y, 85.60–96.44% for Y1, 79.70–94.52% for Y2 and 53.80–89.79% for Y3. In all cases, for the catalyst load of 1.5 and 2.0 g L^{-1} , the amount of CR removal is almost same after 4 h treatment. Hence catalyst load of 1.5 g L^{-1} was taken as optimum value for the oxidation of CR in all sets of experiment. The effects of catalyst loading on CR oxidation are shown in Fig. 8. It was found that, conversion of the dyes increased with increase in the amount of catalyst to a certain extent and then the conversion remained constant. This is because, as the amount of the catalyst is increased, the number of adsorbed dye molecules also increased due to the increase in the number of active sites. But above a certain limit, the increased number of active

Fig. 6 Effect of reaction time on Congo red oxidation with zeolite Y catalysts (Y, Y1, Y2 and Y3) at 303 K and atmospheric pressure (catalyst load 1.5 g L^{-1} , dye concentration 10.0 mg L^{-1})

Fig. 7 Second order kinetics for Congo red oxidation with zeolite Y catalysts (Y, Y1, Y2 and Y3) at 303 K and atmospheric pressure (catalyst load 1.5 g L^{-1} , dye concentration 10.0 mg L^{-1})

Fig. 8 Effect of catalyst load (Y, Y1, Y2 and Y3) on Congo red (10.0 mg L⁻¹) oxidation at 303 K and atmospheric pressure

sites unable to adsorb the available dye molecules. This increase in catalyst load beyond a certain limit does not increase the catalysis activity and hence oxidation process remain almost constant [49]. Singh et al. [31] had studied the degradation of CR using Cu–Y catalyst and reported that with increase in catalyst load from 0.5 to 1.0 g L⁻¹, the percentage degradation of CR increased from 79.11 to 91.13% (2 h) and further increase in catalyst load result in decrease in degradation to 81%. In the present case, with raw zeolite Y(Y) CR degradation was only 25.57% (Fig. 7) which was increased more than three times with Co(II)-incorporated zeolite Y(Y1)

3.2.4 Effect of dye concentration

To study the effects of dye concentration, the amount of catalysts was taken as 1.5 g L⁻¹ and the CR concentration was varied from 1.0 to 100.0 mg L⁻¹. The conversion of CR in the said concentration range decreases as: 29.09–19.85% for Y, 96.26–48.90% for Y1, 98.06–68.90% for Y2 and 80.12–34.40% for Y3 respectively. The decrease in oxidation of CR with increase in concentration is shown in Fig. 9. The observed decrease in conversion of dye with increase in concentration may be due to the fact that the available surfaces of the catalyst are saturated with the dye molecules. As the concentration of the dye is high, more dye molecules will be adsorbed on the catalyst surface and thus the active sites of the catalyst molecules will be reduced. Also with increase in dye concentration, the number of dye molecules increased and the competition with the hydroxyl radical concentration also increased and hence the removal rate of dye decreased [50]. Dafare et al. [51] had observed the degradation efficiency of CR in different initial concentration (50–200 mg L⁻¹) using Fe₂O₃ (2g L⁻¹) as catalyst and found that degradation process decreased with increase in concentration. According to

Fig. 9 Congo red oxidation at different concentration with Y, Y1, Y2 and Y3 (1.5 g L⁻¹), 303 K and atmospheric pressure

them, at higher dye concentration, path length is reduced and production of hydroxyl and superoxide radical is less, which, in turn, decreases the photodegradation process.

3.2.5 Effect of pH

Congo red, an anionic dye, is very sensitive dye to pH. It develops blue colour at pH < 5 and deep red colour at pH > 10. Thus the effects of pH on CR oxidation were studied in the pH range 6.0–10.0. Oxidation of CR in the pH range 6.0 to 10.0 with catalyst load of 1.5 g L⁻¹ was carried out at 303 K and atmospheric pressure for the dye concentration of 100 mg L⁻¹. As shown in Fig. 10, with all metal incorporated zeolite Y, the degradation of CR increased with increased in pH reaches a maximum value at pH 6 and thereafter it decreased and become almost constant. Afkhami and Moosavi [52] reported similar type of result showing that highest adsorption of CR was found at pH 5.9 that decreased considerably up to pH 7.6.

It was observed that increase in pH had a negative influence on the oxidation of anionic dyes like CR. This may be due to the reason that large number of H⁺ ions present in acidic medium facilitates the adsorption of anionic dyes. But as the pH of the solution increased, the negatively charged catalyst surface repels the anionic dye and thus progressively decreases the oxidation of anionic dye (congo red) at higher pH. In addition, to determine the concentration of leached metal ion, the solutions were analyzed at different pH value (2.0, 4.0, 6.0, 8.0 and 10.0) by AAS measurement. It was observed that metal ion concentration decreased from 15.72 to 0.024 mg L⁻¹ for Co(II)–zeolite Y (Y1), 17.35 to 0.082 mg L⁻¹ for Ni(II)–zeolite Y (Y2), 16.85 to 2.61 mg L⁻¹ for Cu(II)–zeolite Y (Y3) with increase in pH value. Thus in acidic medium the leaching of metal ion was highly significant. Hence all the experiments were carried out at the natural pH of the respective dye solution.

Fig. 10 Effect of pH on oxidation of Congo red over Y, Y1, Y2 and Y3 (1.5 g L^{-1}) with dye concentration 10.0 mg L^{-1} at temperature 303 K and atmospheric pressure

Fig. 11 Effect of temperature on oxidation of Congo red over Y, Y1, Y2 and Y3 (1.5 g L^{-1}) with dye concentration 10.0 mg L^{-1} at pH 4.0 and atmospheric pressure

3.2.6 Effect of temperature

With a fixed catalyst load of 1.5 g L^{-1} , CR oxidation (10.0 mg L^{-1}) varied from 21.55 to 28.17% for Y, 95.74–98.85% for Y1, 92.33–95.13% for Y2 and 67.22–84.05% for Y3 as the temperature increased from 293 to 323 K. As shown in Fig. 11, all the zeolite catalysts showed positive effects on conversion of the dye and reached higher values at higher temperature. The increasing oxidation with temperature may be due to the fact that with rise in temperature, the mobility of the reactant molecules increases and so without the transport limitation they can reach the catalyst surface and lead to the increase in oxidation of the dye. Kundro et al. [39] had also observed the similar trend as in the present study for CWAO of CR using Fe-exchanged zeolite when the temperature was varied from 50 to 100°C . They reported that maximum conversion of CR (99.1%) was observed at 100°C in 4 h whereas the dye removal decreased gradually

with decrease in temperature. Endothermic adsorption of CR on Ca-bentonite was also reported by Lian et al. [53].

Nezamzadeh-Ejhieh and Shahriari [54] reported that higher temperature reduced the solubility of oxygen in water and produced significant evaporation of the reacting solution. Thus the temperature more than 313 K was not recommended by them. Therefore, in our present case normal room temperature (303 K) was taken as experimental temperature, although the performance of degradation processes was not as fast as at higher temperature.

3.3 Stability of the catalyst

The reusability of the metal incorporated catalysts was tested on the basis of its catalytic activity up to three consecutive runs. For this, the reaction mixtures, after the completion of the reaction, were centrifuged and the solid material was separated. The material was then agitated with water for 2 h in a water bath shaker to remove the dye sticking to the support. After that the catalysts were dried in oven at 393 K and were used for the next run. All the catalysts showed almost the same activity (decreased by 4–5%) for the oxidation of Congo red up to the three consecutive runs.

3.4 Monitoring dye oxidation with COD measurement

The COD of the remaining dye solution after degradation was measured to examine whether the dye actually mineralized on CWAO process or the decolorization of the dye was due to some other factors. In the present case, the COD load of Congo red after completion of the reaction over zeolite Y catalysts (catalyst load 1.5 g L^{-1} , dye concentration 10.0 mg L^{-1} , temperature 303 K, pressure 1 atm, pH 6.4) decreased from 1450 to 930, 65, 20 and 135 mg L^{-1} for the reaction time of 0–300 min and overall reduction of COD was 35.86, 95.51, 98.62 and 90.70% for Y, Y1, Y2 and Y3 respectively. The oxidation of CR under identical condition was 25.48, 95.90, 97.54 and 87.79% for Y, Y1, Y2 and Y3 respectively as reported earlier. All the experiments done above showed more than 90% COD reduction using metal incorporated catalysts, which proves that decolorization of the dye solution was achieved through oxidative degradation [55]. It was reported earlier in the literature that mineralization of nitrogen present in the dyes converted into NH_4^+ , NO_3^- or N_2 , sulphur into SO_4^{2-} , C, H and O into CO_2 and H_2O respectively [56, 57]. Reduction of COD as a confirmation of degradation of dyes have made by a large number of workers. Dutta et al. [55] observed 89% removal of COD for methylene blue using Fe^{2+} – H_2O_2 in a Fenton type reaction at room temperature and atmospheric pressure. Apollo et al. [58] had observed that

integrated AOP-AD system for the treatment of MB using TiO_2 /zeolite achieved 81% colour removal and 80% COD reduction respectively. On the other hand, Kondru et al. [31] have found 58% removal of COD for Congo red at pH 7, 90 °C using 0.6 mL H_2O_2 /350 mL solution and 1.0 g L^{-1} Fe exchanged zeolite Y as catalyst.

4 Conclusion

Herein, we have incorporated Co(II), Ni(II) and Cu(II) ion on zeolite Y via wet impregnation method. The results showed that all the metal incorporated catalysts could be promising catalysts for the oxidative degradation of the anionic dye (Congo red). The successful incorporation of metal ions into zeolite Y was confirmed by the various characterization methods (AAS, CEC, FTIR, XRD, SEM, and BET surface area). Among all the catalysts, Ni(II)-zeolite Y showed higher catalytic activity for the oxidation of congo red using a catalyst load 1.5 g L^{-1} , dye concentration 10.0 mg L^{-1} , at temperature 303 K and 1 atm pressure. In addition, considering low leaching of metal ion at near neutral pH, the natural pH of the dye was taken as optimum pH. All the reactions followed second order kinetics with good linearity. Again more than 90% reduction in COD value with all the metal incorporated catalysts indicates degradation of the dye to the simple molecules through CWAO process. Also the catalysts could be used successfully up to three consecutive runs. We hope that this work will provide valuable insight on the works of degradation of various similar dyes.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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