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Degradation of Rhodamine B by using Co-ZSM-5 Catalyst

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ABSTRACT: Co-ZSM-5 catalyst was prepared using ion exchange method. The prepared catalyst was characterized using XRD and SEM techniques. Eco friendly photo catalytic degradation of Rhodamine B was carried out using this synthesized heterogeneous environmentally benign catalyst. Sunlight was used for irradiation and using H_2O_2 100% abasement of the dye was achieved within the time duration of 60 minutes. The effect of recyclability of the catalyst and pH effect on the Rhodamine B dye degradation were also examined and the results are discussed.

KEY WORDS - Catalysis, cerium, Co-ZSM-5, H_2O_2, photodegradation, solar light, zeolite.

I. INTRODUCTION

The semiconductor oxides have been widely used in photocatalytic reactions [1-3]. This semiconductor metal oxide when supported on a heterogeneous microporous material showcased enhanced activity and has found to be recyclable. They have been the most widely used class of organic dyes such as textile and fibers and paper, dyeing, paint, laser, liquid crystalline displays, and ink-jet printer, etc. Rhodamine B is the important organic contaminants which pose severe threat to the environment owing to its toxic nature. Semiconductor metal oxide is versatile for photolysis of organic contaminants. Among the transition semiconductor metal oxides cobalt showed high activity towards many reactions [4–7]. These metal oxides when supported using a suitable catalytic material exhibited escalated behavior as photocatalyst [6, 7]. It was reported in literatures that Co-ZSM-5 has demonstrated an exorbitant activity as catalysts material [8-10]. The structure of the typical pollutant Rhodamine B dye is given in the Fig. 1.

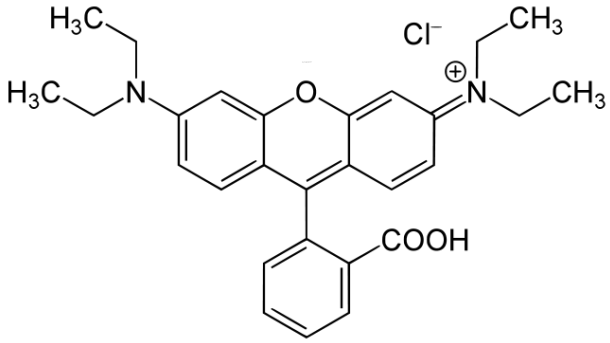

Fig. 1Structure of Rhodamine B dye

Hence the present work deal with the synthesis and characterization of cobalt loaded zeolite, ZSM-5 and test its activity for the degradation of Rhodamine B dye using the synthesized catalysts along with other semiconductor metal oxides in the presence of sunlight. Various factors influencing the photocatalytic activities like the pH and recyclability were also studied.

II. EXPERIMENTAL

2.1 Materials:

Rhodamine B (Merck), sodium hydroxide (99.9 % Merck), hydrochloric acid (37%; Merck), 30% H_2O_2, cobalt chloride, cerium nitrate hexahydrate (99.99 %)

2.2 Synthesis of ion exchanged catalysts:

Co-ZSM-5 and Ce-ZSM-5 was synthesized by incipient wet impregnation method using the heating magnetic stirrer. 25 mL of the respective metal salt solution (0.5M) was taken in a round bottom flask and 1 g of ZSM-5was added to it, and continuously stirred for 3 h at 85 °C. It was then filtered and dried in the oven at 75 °C for 3 h. The dried catalyst was used for further characterization. The resulting dried catalyst material was calcined at 550°C for 5h.

2.3 Experimental procedure for photodegradation of Rhodamine B dye:

100 mL of 1 x 10^{-4} M solution of Rhodamine B dye was taken with 0.3 g of the prepared catalyst. The degradation reaction was carried out under solar light with the dye solution containing the catalyst being continuously stirred using a magnetic stirrer. 3 mL of the sample was withdrawn at required time intervals for analysis. The % degradation was calculated using the below formulae

$$\% \text{ degradation} = \frac{Co - C}{Co} X100$$

Where Co = initial concentration of dye
C = concentration of dye after photo degradation.

The experiment was carried out in sunlight between 9 am to 2 pm in the month of January. The digital lux meter LX-101 was used to measure the intensity of the sunlight. During this period, the average intensity of sunlight was 1.2371 x 10^5 lux unit.

2.4 Characterization:

X-ray diffraction study of the catalysts was done by Philips X'Pert model no. PW 3040/60, using Cu Kα radiation (λ = 1.5060 Å).The morphology of the catalyst was studied with scanning electron microscopy using a Hitachi S-4200 electron microscope The photocatalytic degradation of Rhodamine B dye was monitored by using a double beam spectrometer-2203, Systronics.

III. RESULT AND DISCUSSION

3.1 XRD investigation:

The XRD pattern of Co-ZSM-5 is showed in Fig. 2 shows 10°and 30° (2θ values). Crystalline nature of the zeolite was shown in with no amorphous phase. The XRD pattern is similar to the literature reported [3]. The XRD pattern has no additional peaks due to the presence of cobalt. This clearly shows that the semiconductor metal oxide is well dispersed over the surface of the ZSM-5 catalyst.

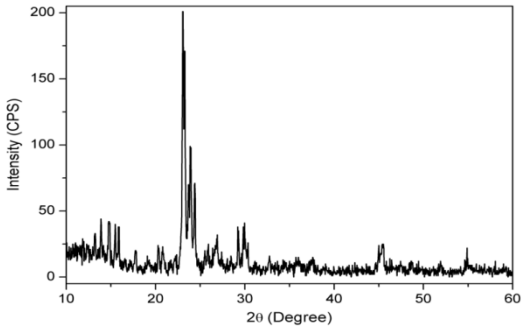

Fig. 2 XRD of Co-ZSM-5

3.2 SEM investigation

The surface morphology of the Co- ZSM-5 were obtained from SEM and shown in the photograph Fig. 3. There is no significant change in the morphology of Co-ZSM-5 due to the incorporation of the metal. The surface morphology is seemed to be maintained without any noticeable change which deciphers to us the crystalline nature of the ZSM-5 remains intact as confirmed from the XRD.

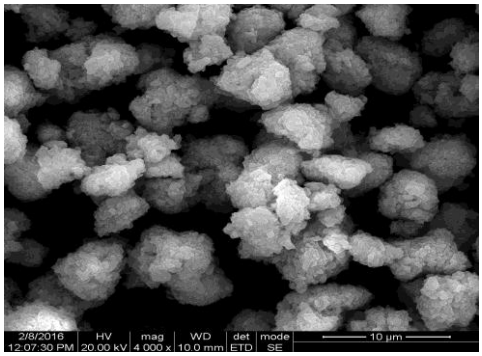

Fig. 3 SEM of Co-ZSM-5

3.3 Photocatalytic activity of various catalysts

Fig. 4 shows the degradation of the Rhodamine B dye over various catalysts. Among the catalysts tested Co-ZSM-5 catalyst showed the highest activity. The band gap of cobalt oxide is 2.4 eV. Photons of visible light have energy from 1.6 eV to 3.2 eV. This semiconductor metal oxide cobalt oxide exhibited comparatively high activity due to the band gap of this metal oxide can able to interact with the visible radiation at 520 nm which is the wavelength region which is equivalent to the band gap of cobalt oxide 2.4 eV. The visible light energy is thus most sufficient to generate electron hole pairs for the degradation of the organic pollutant. The semiconductor metal oxide dispersed on the microporous solid acid material exhibited increased activity in the photo degradation of Rhodamine B dye. This may be due to the higher separation of charges which is facilitated due to dispersion of the active sites over the solid acid catalyst [11, 12]. The degradation was not observed to be vast, hence this photo degradation was planned to be carried in the presence of H_2O_2 along with the catalyst, as it is already reported in literature the $OH^{\cdot}$ Radical is important for the degradation of Rhodamine B dye molecule [13]. Hence the study is carried out using 0.5 mL of hydrogen peroxide as it was the optimum concentration used for Rhodamine B dye degradation in the previous studies [14].

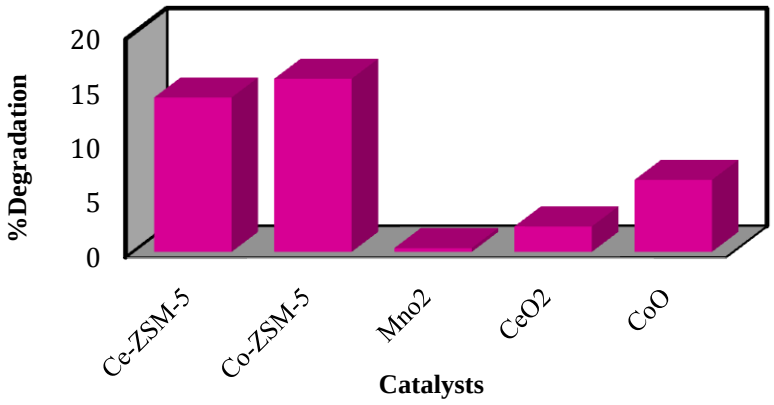

Fig. 4 photodegradation of Rhodamine B dye over various catalysts

3.4 Time on stream

The time on stream was also studied and it was observed that at 1 hour duration itself 99.9 % degradation occurred and it was sustained with very negligible increase in the degradation of the dye molecule. Hence 1 hour duration is considered to be the optimum time for the degradation of the dye molecule. The mechanism of the reaction is proposed in the scheme 1. The presence of hydrogen peroxide prevents the electron hole recombination, it in itself generate hydroxyl radicals which should be the reason of the observed high degradation.

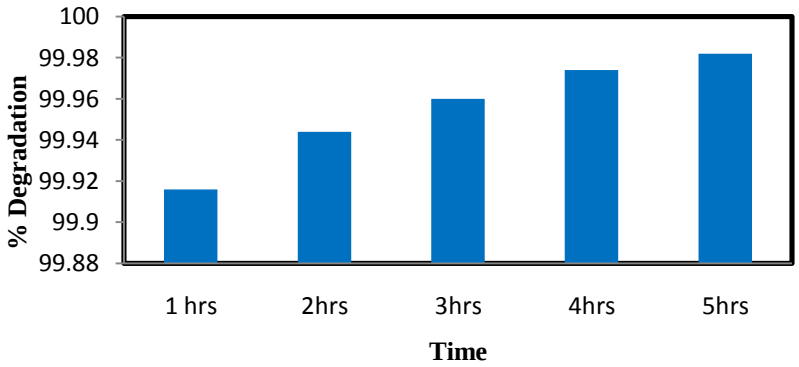

Fig. 5.Time on stream study of degradation of Rhodamine B dye with Co-ZSM-5 and H_2O_2

$$CoO + h\nu \longrightarrow h^+ + e^- \quad \ldots (1)$$
$$h^+ + H_2O \longrightarrow {}^{\bullet}OH + H^+ \quad \ldots (2)$$
$$e^- + h^+ \longrightarrow \text{Heat} \quad \ldots (3)$$
$$H_2O_2 + h\nu \longrightarrow {}^{\bullet}OH + {}^{\bullet}OH \quad \ldots (4)$$
$$H_2O_2 + {}^{\bullet}OH \longrightarrow H_2O + HO^{\bullet}_2 \quad \ldots (5)$$

Scheme 1 Degradation of Rhodamine B by using Co-ZSM-5 and H_2O_2

3.5 Recycling of the catalyst:

The active Co-ZSM-5 is found to be recyclable as its nature being heterogeneous; the catalyst after the first run was filtered washed with deionised water several times, dried in hot air oven and calcined at 500˚C for 2h and reused. The results of the first and second recycle are shown in the Fig. 6. The recycled catalyst was proved to be very active with marginal declination in its activity. The second time when it is recycled its efficacy diminished significantly. This proves the importance of the catalyst role in the reaction of degradation of the Rhodamine B dye is vital. Only H_2O_2 presence together with the second time recycle catalyst impairs the degradation. The percentage degradation with hydrogen peroxide alone is comparable with the value already reported [14]. The unique structure of the support ZSM-5 should play an active role for this observation. Its structure must have prevented the step 5 of the scheme 1 to happen for that per oxy free radical would form which is a weak oxidizing agent when compared with hydroxyl free radical.

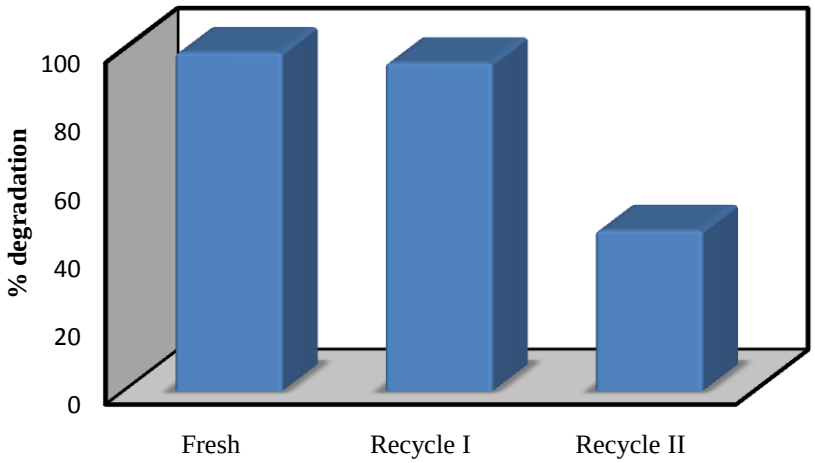

Fig. 6 Effect of recyclability of the photo catalyst Co-ZSM-5

3.6 pH study

The photolysis of Rhodamine B dye was carried out in various pH range and the results are shown in the Fig.7. At neutral pH the degradation was found to be optimum. At the acidic pH which was adjusted at 4 using HCl decrease in the degradation was notices at the basic pH also decrease in the degradation was noticed. At low pH the dye being cationic could be hindered for degradation reaction by the presence of H^+ ions due to columbic repulsion. At higher pH the recession in activity may be due to the presence of excess of hydroxyl ions, which inhibits the degradation process of interaction of dye with hydroxyl free radicals.

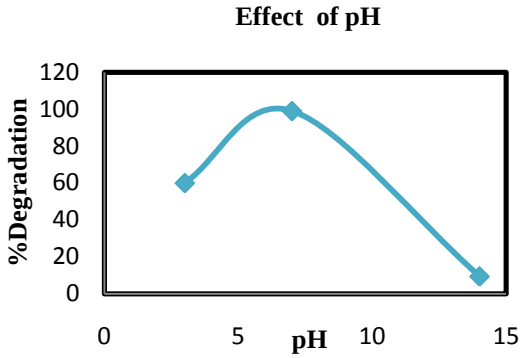

Fig. 7 Influence of pH on Rhodamine B dye degradation

IV. CONCLUSION

The above observation clearly showed that Rhodamine B dye could be 99.9 % degraded within 1 hour using solar light which is abundant and 0.5 mL of hydrogen peroxide which was prerequisite for efficient degradation over 0.3g of Co-ZSM-5 catalyst for 100 mL of 1 x 10^{-4} M solution of Rhodamine B dye. The catalyst being heterogeneous was successfully recycled for the first time without much change in the activity. Neutral pH was found to be suitable for this optimum degradation of Rhodamine B dye.

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