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Kinetics and Photodegradation Study of Congo Red using Mg with Ti/Al Co-Doped ZnO Nanocomposite under UV Light

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ZnO nanocomposites co-doped with dopants like Mg with Ti or Al were prepared and assigned as ZnO-A and ZnO-B. All the nanocomposites were characterized by XRD, SEM and EDX and its utility towards the photodegradation of Congo red is studied. The present study was carried out in 30 W mercury lamp fitted in batch photoreactor and the effect of decomposition was measured in UV-absorption. Nanocomposite with combination of Ti dopant (ZnO-A) exhibited effective degrading ability to aqueous Congo red solution. A solution of 100 ppm of above concentrated ZnO nanocomposite solution was reduced nearly to 5ppm within 5 h. The photodegradation kinetics revealed that the photodegradation of aqueous Congo red follows first order reaction and showed quite comparable degradation effeciency with earlier reports.

Keywords: ZnO nanoparticles, Congo red, Photodegradation, Kinetics.

INTRODUCTION

The present-day researchers have paid much attention to environmental remediation efforts caused by dyestuffs and other commercial colourants. Mainly the efforts focus on removing dye-stuffs from the discharges of various industry units like textile, kraft mills, dye processing units, *etc*. The discharges from these industries causes serious environmental pollution problems due to toxic and potential carcinogenic substances present in their aqua sphere [1]. Public concern arises over these pollution causing pollutants and makes more stringent international environmental standards. A new innovative method is important for the treatment of persisting organic chemicals and converting them into harmless compounds in water. To degrade the colour of dye contaminated water includes many conventional technologies such as physical methods (primary) like adsorption and flocculation [2], biological methods (secondary) [3] and chemical methods like chlorination and ozonization [4]. However, these non-destructive techniques, transfers only the non-biodegradable matter into sludge, results in another pollution, leading to additional treatment. On comparing the classical approaches with advanced oxidation processes (AOP) technique, the later attracted many scientists, for their easy operations and less residue formation. Of all the techniques employed in the AOP approach, UV photolytic technique is considered to be most reliable [5].

In the last few decades, increasing interest has been observed in the development of new compounds to satisfy the demands of the technological advancements. Zinc oxide is one of the best photocatalyst, characterized by a band gap ~3.37 eV and massive excitation binding energy of 60 meV. ZnO is most widely applied in the photolytic process of organic and inorganic compounds, due to its non-toxicity, thermal stability, chemical stability, excellent performance in the UV range of the electromagnetic radiation, and their low cost-environmentally friendly nature [6]. ZnO materials have very high electrical resistivity, as thermoelectric application is considered but it may be reduced by doping, thus doping plays an important role in improving its thermoelectric properties [7]. As previously reported literature Al doped ZnO found to be one of the best thermoelectric materials for high temperature thermoelectric application [8]. Furthermore, an earlier report brings interesting buffer layer fabrication in solar cells employed to minimize energy band in different absorbing materials [9]. It is achieved when magnesium doped with ZnO produces wide band gap tunable nanomaterial influenced by the amount of Mg used for doping [10]. But, the influence of various co-doping metals on the photocatalytic property of ZnO has not been reported.

In most of the cases, zinc oxide has better performance in photolysis than TiO_2 [11], this is due to it has numerous surface-active sites which results in efficient photodegradation of dyes and effectively generates H_2O_2. Apparently, the effectiveness further more improved by doping the metal and non-metal on it. Numerous investigations were available for the doping of TiO_2 on ZnO and has been known that degradation of aqueous dye solution increases when concentration of dopants is more. Not much work has been reported in codoped TiO_2/ZnO system. In search of new nanocomposite, introduction of co-doping of Mg with TiO_2/ZnO and Al/ZnO systems have been investigated. To study the effectiveness of Mg co-doped TiO_2/ZnO clearly, another system Al/ZnO without TiO_2 has been selected and co-doped with magnesium. This work is focused on the development of nanomaterials which can be used for the effective removal of colourants from aqueous media by photodegradation. The aqueous dye solution that has been chosen for the present investigation is Congo red dye. Photodegradation of Congo red dye in aqueous solution carried out under UV light. Accordingly, it will be interesting and worthwhile to study the photodegradation of Congo red dye by doped ZnO and to discuss the kinetics and thermodynamic parameters associated with it.

EXPERIMENTAL

Congo red (CR) of 95 % purity and metal salts required for the preparation of ZnO nanocomposite were purchased from Sigma-Aldrich. The aqueous solution of congo red dye (100 ppm) was prepared in double distilled water.

Preparation of Mg and Ti/Al co-doped ZnO nanoparticles: In this study, a co-precipitation reaction was carried out using zinc nitrate hexahydrate with transition metal salts of magnesium nitrate hexahydrate and titanium (IV) isopropoxide/aluminium nonahydrate. The precipitation is completed by adding a solution of NaOH. The resulted white precipitate is washed, dried and is calcinated at 450 ºC for 3 h. The prepared nanocomposites are collected and subjected to further characterization studies.

Photodegradation: The sample is prepared by dissolving about 10 mg/L of Congo red dye in 50 mL of distilled water with 40 mg of Mg and Ti/Al co-doped ZnO nanomaterials. The samples were placed under UV irradiation for the degradation of dye and measured for every 30 min and process is continued for 3 h. The decomposition effect was measured by UV-absorption measurement supported with a 30 W mercury lamp UV light sources.

RESULTS AND DISCUSSION

XRD analysis: The XRD studies outlines the two types of Mg and Ti/Al codoped ZnO nanocomposites as shown in Fig. 1. Each spectrum of crystalline ZnO nanocomposites revealed the hexagonal wurzite structure which were well supported by XRD peaks [12]. The presence of peaks at 31.67º, 34.41º, 36.20º, 47.50º, 56.50º, 62.8º, 67.90º and 69.11º corresponds to (100), (002), (101), (102), (110), (103), (112) and (201) planes were observed. Obviously, the peaks are sharp and strong in nature, which indicates effects of impurities are negligible. The inclusion of dopants decreases the intensities continuously which were observed in peaks (100), (002) and (101). The average particle sizes of nanocomposites were calculated using Scherrer′s formula and found to be 37 and 34 nm, respectively for ZnO-A and ZnO-B [13].

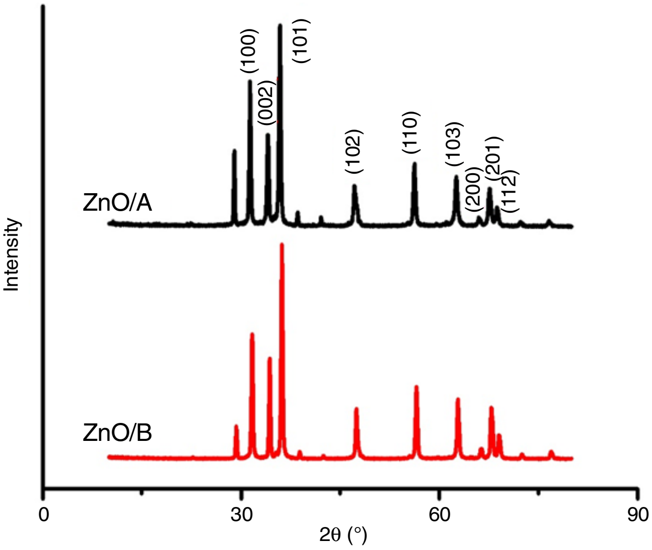

Fig. 1. XRD spectra of photocatalysts ZnO-A and ZnO-B used

SEM-EDX analysis: The images of SEM and EDX of ZnO co-doped with Mg and Ti/Al nanoparticles are shown in Fig. 2. The SEM images shows the non-uniform size and spherical morphology of the prepared nanoparticles [14]. The sizes of ZnO-A and ZnO-B nanoparticles were calculated as 85 and 60 nm, respectively. The elements of Zn and O were clearly seen in the EDX spectra of ZnO co-doped with Mg and Ti/Al. In addition, the spectrum also indicates the presence of host lattice of Mg and Ti/Al, and evidently shows the impurities absence which correlates well with the XRD analysis [15]. The greater peak in a spectrum gives the evidence that the elements of nanomaterials were in high concentration [16].

Kinetics of photodegradation of Congo red: The nanocomposites of ZnO-A and ZnO-B were applied as the photocatalysts for the degradation of Congo red in aqueous medium. It was confirmed that ZnO-A showed better degradation efficiency than ZnO-B (Fig. 3). The higher efficiency exhibited by ZnO-A is due to the doping element present in them [17]. It may also be assumed that vacancies created by oxygen numbers available in their structure was responsible for the degradation of Congo red and at times that excessive p-type metal oxide could cover up the surface of photocatalysts. This effect is measured as one of the important factors than morphology and surface of catalyst [18].

The photodegradation mostly follows the kinetic model given by Langmuir-Hinshelwood, which is proportional relation between rate of photochemical degradation to covered surface of photocatalyst [19].

$$\text{Rate} = -\left(\frac{dC}{dt}\right) = K_r\theta = \left(\frac{K_rKC}{1} + KC\right)$$

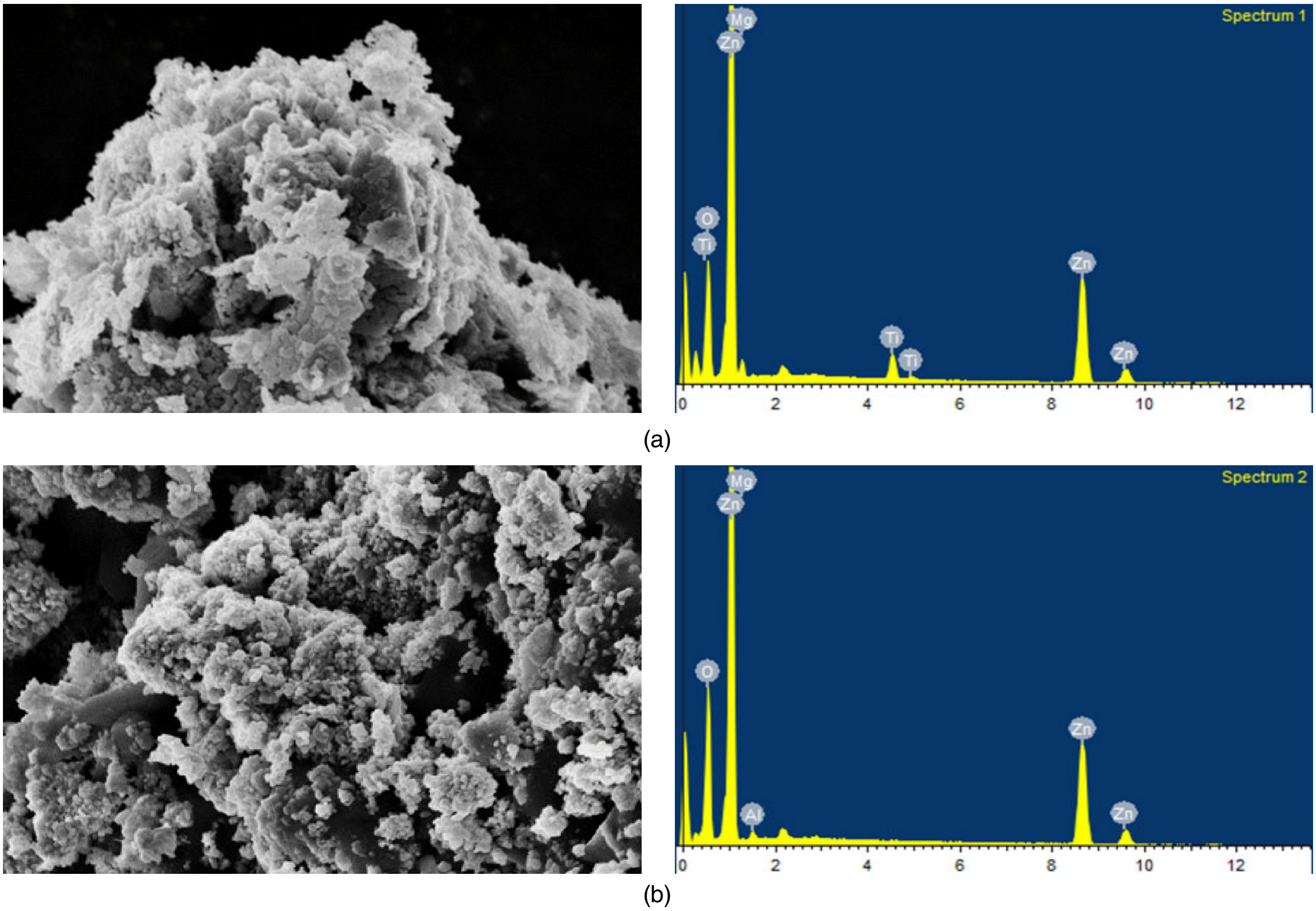

Fig. 2. SEM and EDX of photocatalysts ZnO-A and ZnO-B

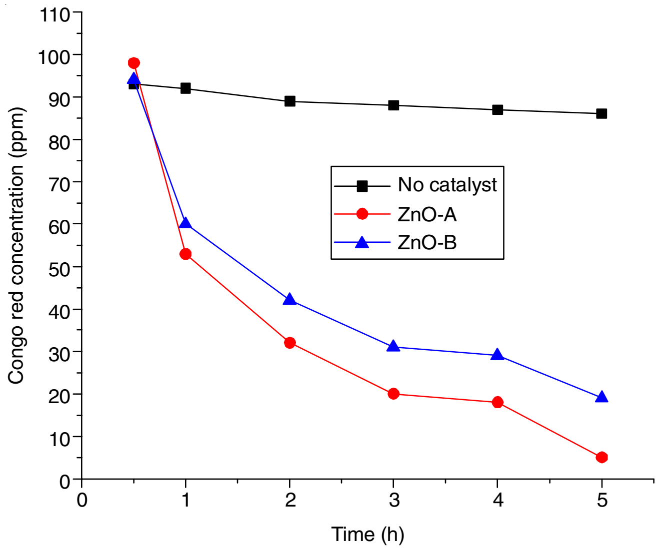

Fig. 3. Photodegradation of aqueous Congo red using ZnO-A and ZnO-B as photocatalysts

At very low concentration, KC <<< 1

$$-\ln\left(\frac{C}{C_o}\right) = K_{app}$$

where, K_r = rate constant; K = adsorption coefficient of reactant on the surface of catalyst; and C = concentration of reactant (Congo red).

On plotting $-\ln(C_o/C)$ *versus* irradiation time for two catalysts, straight lines were obtained is shown in Fig. 4. This shows that order of the photodegradation of Congo red in aqueous medium is first order type (Table-1).

Effect of pH on the photodegradation of Congo red: The photocatalytic reactions mainly use semiconducting metal oxides like ZnO and TiO_2 because of its amphoteric properties

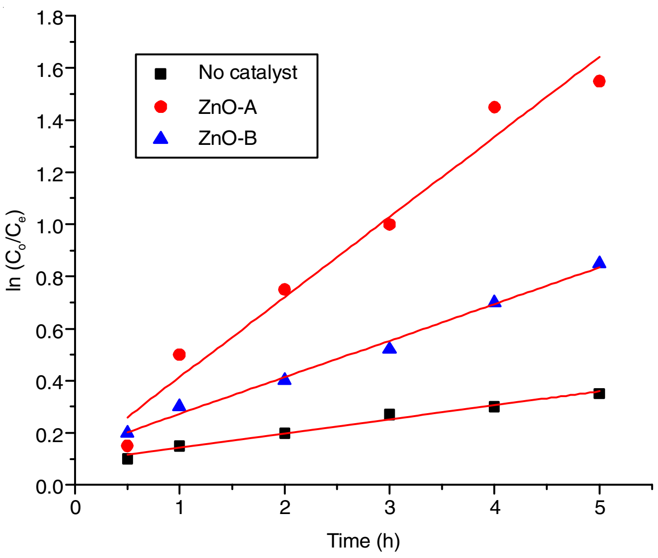

Fig. 4. Kinetics of photodegradation of aqueous Congo red using ZnO-A and ZnO-B as photocatalysts

TABLE-2
COMPARISON OF CONGO RED PHOTODEGRADATION ON UV IRRADIATION BY NANOCOMPOSITES WITH EARLIER REPORTS

Catalyst	Initial dye conc.	Light source	Time (min)	Degradation (%)	Ref.
WO_3-TiO_2/AC	10	500 W-Hg lamp	120	95.12	[24]
CuO	20	18 W-UV lamp (256 nm)	210	67	[25]
ZnO-CdS	10	250 W-Hg lamp	100	88	[26]
$Zn_{1-XCuXS}$	5	40 W-Hg lamp	120	99	[27]
$Zn_{1-XNiXS}$	5	40 W-Hg lamp	120	95	[27]
Ag/TiO_2	30	400 W-Hg lamp	30-150	100	[28]
TiO_2-Degussa P-25	55	Hg lamp-254 nm	480	100	[29]
ZnO-A	10	30 W- Hg lamp	180	92.14	This study
ZnO-B	10	30 W- Hg lamp	180	83.57	This study

TABLE-1
KINETIC DATA OF CONGO RED PHOTODEGRADATION ON UV IRRADIATION IN PRESENCE OF PHOTOCATALYSTS ZnO-A AND ZnO-B

Catalyst	k	R^2	Photodegradation ratios (%)
Without catalyst	0.0539	0.978	74.28
ZnO-A	0.3074	0.963	92.14
ZnO-B	0.1405	0.990	83.57

[20]. The variations in pH of reaction medium has a tendency to alter the properties of this metal oxides [21]. These variations in pH changes in the surface charge distribution and also the sizes of the nanoparticle aggregates. Photodecomposition of Congo red dye in aqueous medium carried out under UV light by photocatalysts ZnO-A and ZnO-B. Further, dispersion of particles of photocatalysts in aqueous medium and the adsorption of Congo red on the surface of photocatalysts will also be affected by pH of the solution.

The photodegradation of Congo red using ZnO-A and ZnO-B was carried out in different pHs. The effect of pH on the efficiency of photocatalytic degradation of Congo red is shown in Fig. 5. It is clear that the pH has no characteristic effect on the efficiency of photocatalytic degradation of Congo red.

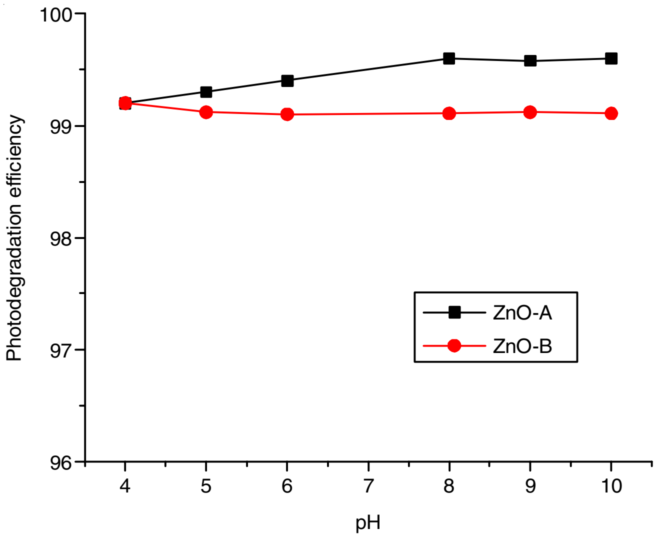

Fig. 5. Effect of pH in the photodegradation of aqueous Congo red using ZnO-A and ZnO-B

As per the previous reports [22], photocatalytic degradation of Congo red using ZnO or TiO_2, an optimum pH of 7 was used. The results get even better, when it was changed from acidic to neutral value. The photodegradation increases by many folds in the alkaline region due to the fact that at higher pH, the recombination of photoexcited electron-hole pair is reduced and availability of more OH^- and $^{\bullet}OH$ [22]. In case of TiO_2, a decrease in the photocatalytic efficiency has been observed at higher pH values. This could be attributed to the repulsion phenomenon between the hydroxyl ions and the negatively charged surface of TiO_2 [23].

Earlier reported works including different photocatalysts were compared with this study for degradation of Congo red dye (Table-2). As can be seen that photocatalytic degradation of Congo red dye by using different photocatalysts such as WO_3-TiO_2/AC, CuO, ZnO-CdS, $Zn_{1-x}Cu_xS$, $Zn_{1-x}Ni_xS$, Ag/TiO_2 and TiO_2-Degussa P-25 [24-29]. ZnO-A and ZnO-B photocatalysts provides a short-period degradation of CR dyeunder UV-light. According to Table-2, ZnO-A and ZnO-B photocatalysts maybe a best option for wastewater treatment.

Conclusion

The potentialities of ZnO nanocomposites with different dopants ZnO-A and ZnO-B in the photocatalytic degradation of Congo red in aqueous medium were studied. ZnO-A found to be effective in the photocatalytically degradation of Congo red even at different pH values. Despite the oxygen vacancies dominating role over the morphology and surface area, a significant increase in effeciency was observed due to dopants Mg and Ti/Al to ZnO nanoparticles. The photodegradation of Congo red in water samples catalyzed by ZnO-A and ZnO-B were observed to follow Hinshelwood first oreder kinetics. The degarading effeciency of co-doped nanocomposites quite comparable with earlier reports.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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