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Efficacy of Mn-doped ZnO towards Removal of Congo Red Dye under UV Exposure: Isotherm, Kinetics, Thermodynamics and Optimization Study

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ABSTRACT

Discharge of synthetic dyes from industries without treatment leads to major environmental problems. Present research highlighted the Mn-doped ZnO along with UV-induced photo degradation of Congo red (CR) dye through batch study. The synthesized Mn-doped ZnO (MDZO) was characterized by Transmission electron microscope (TEM) and Fourier transform infrared spectroscopy (FTIR). The results revealed that MDZO along with UV exposure degraded the CR dye up to 99.3% at concentration 4 mg/L, pH (7), adsorbent dose (0.6 g/L) and contact time (30 min). The degradation data nicely fitted with pseudo-secondary kinetics and the thermodynamic study suggest the said reaction is exothermic in nature. A statistical method, central composite design (CCD) was used to screen out the optimized condition of dye degradation. The interactions of main factors and optimal conditions were also evaluated by 3D surface plots. The statistical output clearly demonstrates that the dye degradation data is nicely fitted with very high goodness of fit and F value (86.19). Present research clearly suggested that Mn-doped ZnO along with UV could be an effective treatment towards degradation of Congo red dye.

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INTRODUCTION

Huge amount of industrial waste water discharges from varieties of industries such as paper and pulp, printing, paint, pigment etc. (Bhad et al. 2022; Unal et al., 2019; Chowdhury and Saha, 2010). The organic pollutants are dangerous for the environment which is associated with toxic -N=N- azo group as, functional group (Ahmad and Alrozi, 2011). The contamination of synthetic dyes is a serious health hazard due to its eco-toxicological effects and bioaccumulation capability in wildlife (Saha et al., 2010). Waste water containing a large amount organic solid is discharged into rivers that are not applicable for domestic and agricultural purpose. This dye containing industrial waste water directly discharged into the natural water body and subsequently causes many toxicological effects due to their carcinogenic, mutagenic and allergic effects (Akar and Özcan, 2009).

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The main problem arise from dyes in natural aquatic body is that they prevent sunlight from entering in water which again cause insufficient photosynthesis that subsequently prevent the growth of both aquatic flora and fauna (Malik et al., 2007). Previous literature (Sadia et al. 2021; Akar and Özcan, 2009; Kiran et al., 2009) also highlighted that dye molecules can be broken down into many carcinogenic fragmented products which causes skin, eye and other organ irritation along with respiratory problem (Allen and Koumanova, 2005; Das et al., 2013). Toxic nature of Congo red dye in waste water has been recognized as a dangerous health problem and therefore, removal of this dye is highly essential. Till recent time, different effective technologies were developed to remove dyes from waste water which drew great attention over the last two decades (Lim and Lim 2019; Rafq et al. 2019). Recently, the effective several methods such as ion exchange, lime softening, membrane filtration, coagulation, precipitation, advanced oxidation process and adsorption etc. have been applied for removal of ~~colour~~ dyes from contaminated water. However, all the above methods are costly, time consuming and generate secondary sludge. Therefore, it is extremely important to develop an effective and efficient method for removal of dyes from aqueous solution. On the other hand, the advanced oxidation process (AOPs) is designed to remove environmental organic and inorganic pollution which has become the focus of many researchers [Karunakaran et al., 2015; Singh et al., 2015; Saggioro et al., 2015; Andreozzi et al., 1999). Similarly photosynthesis in AOPs is also used for breakdown of organic dyes which creates many environmental organic pollutants [Milenova et al., 2013; Mondal and Mitra, 2012; Rekha et al., 2010; Joseph et al., 2005). However, use of metal oxide is really encouraging. Among them, oxides of zinc are extremely applied as photo-catalyst for degradation of organic dyes under UV-lighting radiation (Musial et al. 2022; Roy and Mondal, 2014; Abdollahi et al., 2012). The literature (Roy and Mondal, 2014; Rekha et al., 2010) also highlighted that the modification of surface of metal oxides leads to increase in the active entry on the surface. Moreover doping of transition metal in ZnO also showed excellent photo-catalytic properties (Cilicia et al., 2019). The surface modification of photo-catalyst leads to enhancement of their activity (Wang et al., 2016). Previous research demonstrated that doping of heavy metals in the semiconducting materials enhance the performance of metal oxide such as doping of Cu, Cd in ZnO (Milenova et al., 2013; Mondal and Mitra, 2012; Joseph et al., 2005) and boron, sulfur and phosphrous doped grapheme (Feng et al. 2020). Similarly, Cr and Sn were dopped in ZnS and ZnO, respectively [29, 30]. Screening out the best condition is the prime objective of the experiment where many operating parameters were run at a time.

In modern time, the normal dye degradation techniques are chemical, physical, and biological methods but these methods are not user friendly (Abdellah et al., 2018). A very promising technique called photo-catalytic degradation is now widely used purification dye contaminated water. Photocatalytic processes involves the excitation of a semiconductor material with an energy source higher than the band gap of semiconductor. Upon excitation electron holes pairs are generated that either recombine or may react with the target substance that may be either an electron acceptor (molecular oxygen) or an electron donor (hydroxide ions) (Sadia et al., 2021). Highly reactive species such as superoxide and hydroxyl radicals are generated during the photo degradation process (Bruno and Antoninho, 2019). These radicals are active that attacks the organic dye molecules and purify the waste water.

At present, an efficient technique, the response surface methodology (RSM) where Central composite design model (CCD) and Box-Behnken model were used to overcome these difficulties (simulation of condition) (Sadhukhan et al. 2016; Das et al. 2016, 2015; Sohrabi et al. 2014). Here Central composite design (CCD) was applied to find out the solute - solvent interaction and the optimum condition of different parameters of this adsorption. The novelty of this statistical model is in reducing the time consumption by less numbers of experiments. Therefore, the main purpose of this study is to synthesize an active compound and the efficacy of the synthesized compound (MDZO) towards degradation of Congo red dye under UV exposure. Particularly,

this method of dye degradation was undertaken because to avoid the residual effect which may create problems during disposal. The kinetics of dye degradation was also assessed by applying various kinetics equations and optimization of dye degradation was also exhausted by applying central composite design (CCD).

MATERIALS AND METHODS

Reagents

Congo red (CR) is the typical anionic azo dye used as the adsorbate in the present study. The reagents such as ZnO, $MnCl_2$, HNO_3, NaOH and congo red were analytical grade and procured from Merck Pvt. Mumbai. The standard solution was prepared by using millipore water and to perform the whole experiments, the intermediate solutions were prepared by the dilution of main solution in required ratio. The pH of CR solution was adjusted by the addition of 0.1 M HCl and NaOH solutions whenever necessary. Experimentally, the zero point charge of MDZO was determined by a series of pH from 2 to 10 by 0.1(M) KNO_3 and NaOH solution.

Dye Solution

The standard stock solution of congo red dye (100 mg/L) and intermediate solutions were prepared by proper dilution by Millipore water. The pH of the experimental dye solution was adjusted by 0.05 (M) NaOH and 0.05 (M) HNO_3 solutions.

Preparation of Mn-dopped ZnO (MDZO)

A special procedure was used for preparation of Mn doped ZnO powder. This particular process is known as successive ions layer adsorption and reaction(SILAR). The Mn doped ZnO powder was separated from glass plate through scratching thin film. The substrate dipped into a cationic and anionic precursor solution successively. For cationic precursor 0.1 M $ZnCl_2$ solution and for anionic precursor 0.075 M NaOH for Mn doping, $MnCl_2.4H_2O$ was prepared. For doping of Mn in ZnO, $MnCl_2.4H_2O$ was dissolved in $ZnCl_2$ solution. The cationic and anionic bath was kept in room temperature and at 70°C with maintaining pH 4.7 and 11.10 (Mondal et al., 2013). The dipping duration of glass plate was five second and properly adjusted for getting desired thick film of required powder. The deposited powder was separated and subjected to ball milling by a planetary ball mill at the rate of 300 rpm for 1h.

Instrument and Software

All the experimental instruments such as pH meter (Systronics), UV visible spectrophotometer (Perkin Elmer λ35), Magnetic starrier (Tarsons) etc. were analytical standard. Ball milling in a planetary ball mill (Fritsch Planetary Ball Mill Pulverisette-5), a highly stabilized and automated Philips (PW 1830) X-ray generator were used. The optimization was screen out by using computerized software CCD in Response surface methodology by design experiment version 7.0.3.

XRD, TEM and FTIR study

The synthesized Mn-doped ZnO was characterized by various analytical instruments such as X-ray diffraction (XRD) [Philips (PW 1830)] with copper target operated (40 kV and 20 mA with radiation λ = 1.5418 Å), Transmission electron microscope (TEM) and Fourier transform infrared spectroscopy (FTIR). The films were heated at 350°C for 2 hours prior to structural characterization.

Experimental procedure

In the batch degradation experiments, the effect of different parameters (i.e., pH, contact time, initial CR concentration, dose of photo-catalyst, and temperature) on degradation of CR

was studied. 100 ml solution of CR was taken in each Borosil beaker of volume 250 ml separately.

Photo-catalytic reaction was carried out in a photo-reactor where the lamp was positioned perpendicularly above the beaker. The distance between the lamp and the glass beaker was 10 cm. The whole photo-catalytic reactor was insulated in a wooden box to prevent the escape of harmful radiation and minimized temperature fluctuations caused by environmental interference. After pH adjustment, a known quantity of MDZO catalyst was added and the CR bearing suspensions was kept under magnetic stirring until the equilibrium was reached. At predetermined times; 5 ml of reaction mixture was collected and centrifuged (4,000 rpm, 15 minutes) in a centrifuge. The absorbance at 497 nm wavelengths of the supernatant was determined using ultraviolet-visible spectrophotometer.

Dye degradation percentage study

The dye degradation was studied by applying the following reaction (1):

$$\%\,\mathrm{Re}\,moval = \frac{(C_0 - C_e)}{C_o} \times 100 \qquad (1)$$

Where, C_o and C_e are the initial and equilibrium concentration, respectively. The residual dye concentration after degradation was evaluated by spectrophotometrically at a particular wavelength where each dye exhibited maximum absorption.

Central Composite Design

The most important statistifcal technique called central composite design (CCD) is widely used in the field of industrial optimization process through regression model (Sadhukhan et al., 2016). Basically, CCD was performed through fitting a second-order model which required minimum number of opering variables. The central composite design consists 2nn factorials, 2n axial runs and accentor runs (Sadhukhan et al., 2016). The runs number will increase with increasing the operating variables (n_0 and the entire design (experimental runs, N) can be express in Eq. (2).

$$N = 2n + 2^n + n_c \qquad (2)$$

Similarly an empirical model was developed to correlate the response of dye degradation process which based on second-order quadratic model. The entire response in the form of dye removal (Y(%)) can be express by the Eq. (3).

$$Y = \beta_o + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \sum_{j=1}^{n} \beta_{ij} x_i x_j + \sum_{i=1}^{n} \beta_{ij} x_{ij}^2 + \varepsilon \qquad (3)$$

Where Y is the percent of dye removal (%), β_0 is the intercept, β_i, β_{ij} and β_{ii} are coefficients of the linear effect, interactions, variables (xi and xj) and ε is error.

RESULTS AND DISCUSSION

Batch degradation study

Effect of initial CR concentration

The degradation behaviour of CR was studied in the concentration range of 4-12 mg/L initially at pH 7.0 and catalyst dose of 0.6gm/L (Fig. 2a). Similarly the impact of dual effect of catalyst dose and contact time with initial concentration on degradation efficiency of CR at constant pH (7) is depicted in Figs. 4c and 4d. In general, the percentage of breakdown of CR by MDZO was decreased with the increasing initial concentration of CR, where maximum

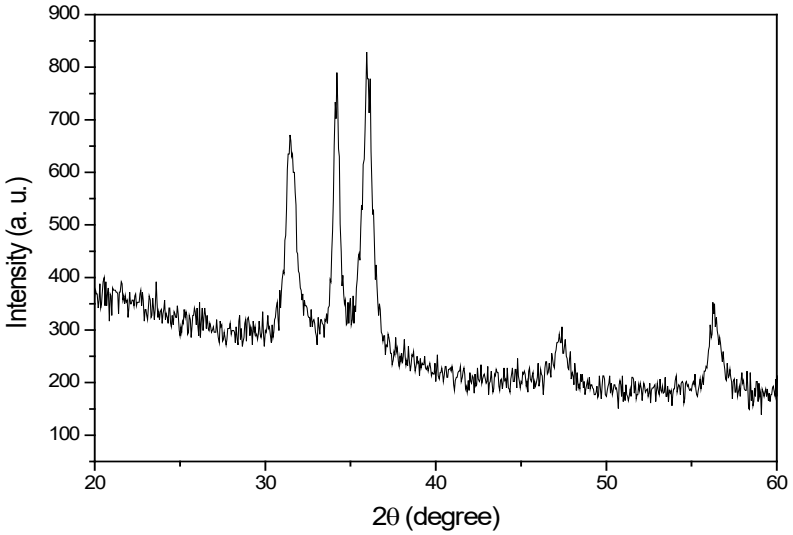

Fig. 1. XRD micrograph of MDZO

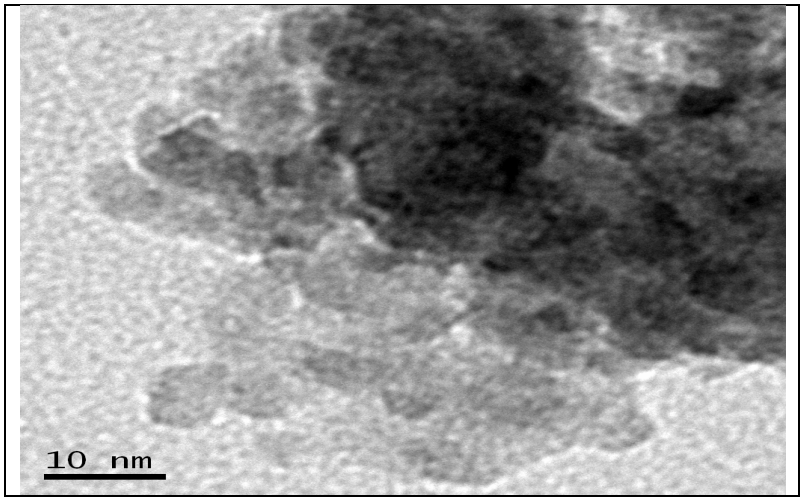

Fig. 2. TEM micrograph of MDZO

degradation was recorded (95%) at 4 mg/L CR concentration (Fig. 2a). With increasing the dye concentration, light penetration is prevented as a matter of fact catalyst does not get sufficient energy to excite the dye molecules. Moreover, with increasing concentration more number of dye, molecules binds with the active surface of MDZO consequently decrease the concentration of hydroxyl radicals which mainly involved for degradation of dye molecules (Daneshvar et al., 2004). Our result is almost similar with the other researchers (Nikazara et al., 2007; Mrowetz and Selli, 2006; Mahmoodi and Arami, 2006; Muruganandham and Swaminathan, 2006; Kartal et al., 2001; Goncalves et al., 1999).

Effect of pH

The pH at the optimum concentration (4 mg/l) of CR. The maximum degradation of 99.22% was obtained at the pH of 7.0. The combined effect of catalyst dose with other parameters on degradation efficiency of CR is depicted in Fig. 4b and 4f. pH of the experimental solution is

extremely important because, the semiconductor surface is positively or negatively charged at low or high zero point charge (zpc) of dyes. pH_{ZPC} is a valuable tool through which charge of the adsorbent surface can be predicted (Akar and Özcan, 2009; Malik et al., 2007; Kiran et al., 2009). The Fig. 2c indicated that the CR degradation rates increased with increasing pH up to 7 and decrease thereafter. Therefore, of this pH (7) dye degradation is suitable and catalyst surface gets activated (Daneshvar et al., 2007; Khodja et al., 2001). Almost similar findings were reported by earlier researchers (Dindar and Içli, 2001; Lizama et al., 2002; Shankar et al., 2004). Wang et al. (2016) also reported the enhanced rate of dye degradation by Fe3O4@ZnO photocatalyst after 60 min UV irradiation while ZnO alone could remove comparatively lower level of dye under the same condition.

Effect of catalyst dose

Various doses (0.2 to 1.0 gL^{-1}) of MDZO were used to measure the impact of catalyst on dye degradation (Fig 2b). Results revealed that dye degradation gradually increased with increasing catalyst dose from 0.2 to 0.6 gL^{-1} (Fig. 2b). However, further increase of catalyst dose, dye

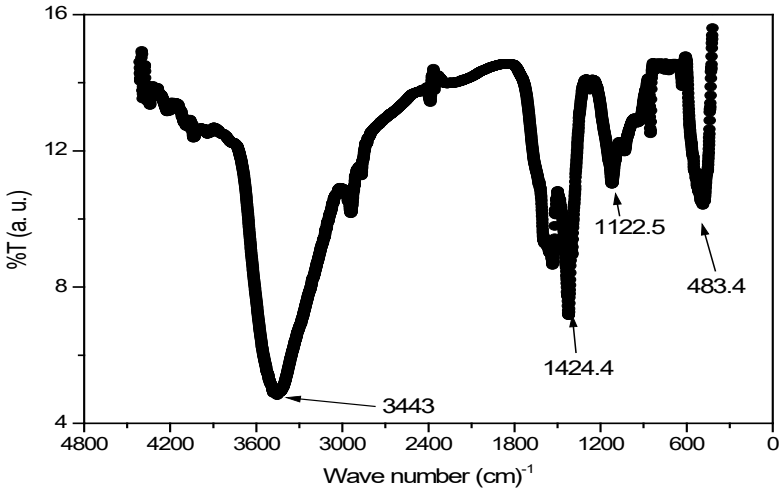

Fig. 3. FTIR of Mn doped ZnO.

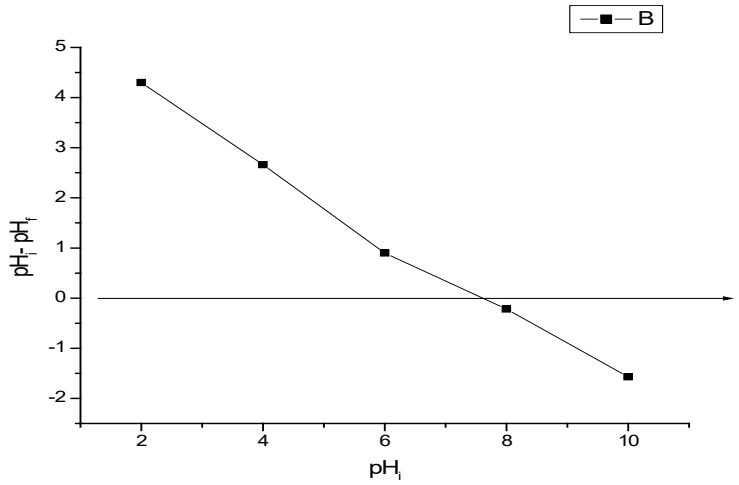

Fig. 4. plot of pHi vs pH_i - pH_f for the measurement of zpc

degradation gradually decreased. This is probably due to coverage of active center of catalyst and UV light could not penetrate (GoUVêa et al., 2000). However, at lower dose, UV light can easily penetrate and activate the active center.

Effect of contact time

The degradation of CR by MDZO with different time interval (15-60 min) at optimum value of CR concentration (4 mg/L) at pH 7.0 and 0.6 gL^{-1} of catalyst dosage is shown in Fig. 2d. The combined effect of CR concentration, catalyst dose and pH separately with contact time are depicted in Figs. 4b, 4d and 4g. The percentage degradation of CR showed a rapid and steady increase up to 30 min, and thereafter, no significant increase was recorded. This is possibly due to equilibrium was reached at 30 min (Fig. 2d). The first degradation of dye at initial stage is perhaps due to availability of active center on the surface of catalyst (Saqib et al., 2013; Das et al., 2013). However, in later stage, catalyst surface is absolutely saturated and dye degradation decreased (Roy and Mondal, 2013; Sokker et al., 2011).

Kinetics of dye degradation

Model analysis

The present work focused on the degradation of congo red by UV induced MDZO. A second order polynomial equation (Eq. 1) was designed with the experimental results and the following equation was obtained:

$$\begin{aligned} Y = {} & +56.382 + 1.1372x_1 + 38.207x_2 + 10.086x_3 + 0.0556x_4 - 0.142x_1^2 - \\ & 2542.741x_2^2 - 0.814x_3^2 - 1.076E-003x_4^2 + 1.563x_1x_2 - 0.081x_1x_3 - \\ & 3.333E-003x_1x_4 + 32.585x_2x_3 + 1.333x_2x_4 + 2.00E-003x_3x_4 \end{aligned} \quad (1)$$

Percentage of CR degradation results was depicted in Table 1. In order to ensure a good regression model, the analysis of variance (ANOVA) was applied and the results are shown in Table 4. The 'model F-value' of 86.19 implied the model was significant. There was only a 0.01% change that a 'Model F-value' this large could occur due to noise. P value of "Prob > F" (< 0.0001, less than 0.05) indicated model terms were significant. The no significant lack of fit (more than 0.01/0.05) showed that the quadratic model was valid for the study. ANOVA model is depicted in Table 4. Again the data of ANOVA output of this quadratic Table 4 clearly indicate that the

Table 1. Experimental factor levels used in factorial design

Independent variable	Factor	Low	High
Initial concentration (mg/L)	X_1	4	12
pH	X_2	5	9
Photocatalyst dose (g)	X_3	0.02	0.10
Contact time (min)	X_4	15	90

Table 2. Model summary statistics for photocatalytic degradation of CR by MDZO

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	2.89	0.7984	0.7648	0.7265	271.29	
2FI	2.83	0.8548	0.7742	0.7063	291.27	
Quadratic	0.90	0.9885	0.9771	0.9393	60.20	Suggested
Cubic	0.43	0.9993	0.9949			Aliased

Table 3. Adequacy of the model tested

Source	Sum of Squares	df	Mean Square	F- Value	P-Value	Prob>F
Mean vs Total	2.318E+005	1	2.318E+005			
Linear vs Mean	791.81	4	197.95	23.76	< 0.0001	
2FI vs Linear	55.97	6	9.33	1.17	0.3667	
Quadratic vs 2FI	132.61	4	33.15	40.80	< 0.0001	Suggested
Cubic vs Quadratic	10.65	10	1.06	5.85	0.0516	Aliased
Residual	0.73	4	0.18			
Total	2.328E+005	29	8028.41			

Table 4. Analysis of variance (ANOVA) for percentage removal of CR by photocatalytic agent MDZO

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	980.39	14	70.03	86.19 significant	< 0.0001
A-conc	608.16	1	608.16	748.53	< 0.0001
B-dose	35.85	1	35.85	44.12	< 0.0001
C-pH	0.38	1	0.38	0.47	0.5047
D-contact time	1.76	1	1.76	2.17	0.1628
AB	0.25	1	0.25	0.31	0.5878
AC	1.09	1	1.09	1.34	0.2661
AD	1.00	1	1.00	1.23	0.2859
BC	20.70	1	20.70	25.48	0.0002
BD	16.00	1	16.00	19.69	0.0006
CD	0.09	1	0.090	0.11	0.7442
A^2	29.88	1	29.88	36.78	< 0.0001
B^2	100.86	1	100.86	124.14	< 0.0001
C^2	55.08	1	55.08	67.79	< 0.0001
D^2	14.64	1	14.64	18.02	0.0008
Residual	11.37	14	0.81		
Lack of Fit	10.65	10	1.06	5.85 significant	0.0516 not
Pure Error	0.73	4	0.18		
Cor Total	991.77	28			

ANOVA result is suitable to navigate the design space. Moreover high F value [86,19] also suggests that the quadratic model is statistically significant. These predicted R^2 value (0.939) is very close to the adjusted R^2 (0.977) value. The adequate precision which indicate a ratio called signal to noise ratio was recorded 31.308 which is greater than 4 means the signal is adequate. Similarly lower value of coefficient of variant also suggests that good precision of the experiments. The relationship between actual versus predicted of CR degradation influents by MDZO is depicted in figure 4c. The actual and predicted values are basically deals with the measured response for a specific run and the data obtained from model, respectively (Montgomery, 1996; Korbahti and Rauf, 2008). On the other hand, the interaction data for dye degradation was obtained from equation 5. The entire results depicted in Table 1. The interactions also graphically presented as photo degradation process (Fig. 4b-4f). Optimization in the form of the possible goals in the

Design-Expert software's is to maximize, minimize, target, in range and set to an exact value (factors only). The plot (Fig. 4h) demonstrates the desirability values of optimization procedure in which the criterion was set as ''maximum" for initial CR concentration, ''minimum" for photo-catalyst MDZO dose, ''in range" for rate and the goal was set as ''maximum" to analyze economically viable optimal condition. From figure 4h, it is clear that the desirable contact time,

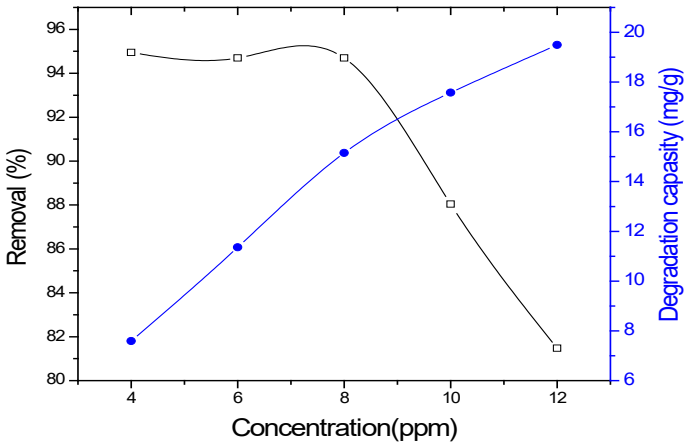

Fig. 5. Effect of concentration on the degeadation of CR by Mn-doped ZnO; contact time: 30 min; dose: 0.6 g/L; pH: 7.0; temperature: 30^{0}C; agitation speed: 150 rpm.

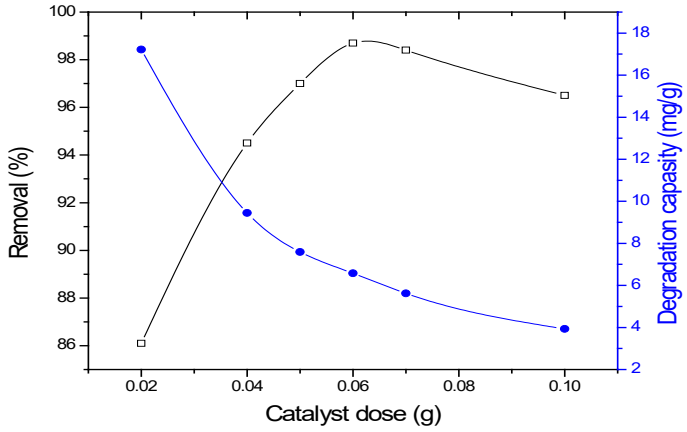

Fig. 6. Effect of catalyst dose on the degeadation of CR by Mn-doped ZnO; contact time: 30 min; concentration: 4 ppm; pH: 7.0; temperature: 30^{0}C; agitation speed: 150 rpm.

Table 5. Summary of parameters for various kinetic models

Kinetic model	Equation	Constants	q_{exp}(mg/g)	q_{cal}(mg/g)
Pseudo first order	$log(q_e - q_t) = logq_e - k_L \frac{t}{2.303}$	R^2 = 0.8195 K_L = 0.03776 min^{-1}	6.62	0.4232
Pseudo second order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$	R^2 = 0.9999 K_2= 1.0108 gmg^{-1} min^{-1}		6.590

q_t and q_e are the amount of dye adsorbed (mg g-1) at time t and at equilibrium and K_L (min^{-1}) is the Lagergren rate constant of first-order degradation and K_2 (g mg^{-1} min^{-1}) is the second-order degradation rate constant.

Table 6. Thermodynamic parameters for removal of Congo Red by MDZO particles

Temperature(K)	$\Delta G(KJmol^{-1})$	$\Delta H(KJmol^{-1})$	$\Delta S(Jmol^{-1}K^{-1})$
293	-11.848		
313	-12.948		
333	-10.828	-37.53	-83.52
353	-6.554		

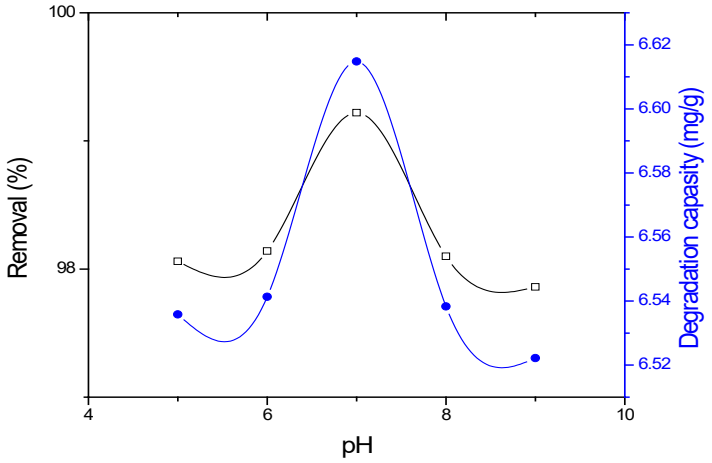

Fig. 7. Effect of pH on the degeadation of CR by Mn-doped ZnO; contact time: 30 min; concentration: 4 ppm; dose: 0.6 g/L; temperature: 30^0C; agitation speed: 150 rpm.

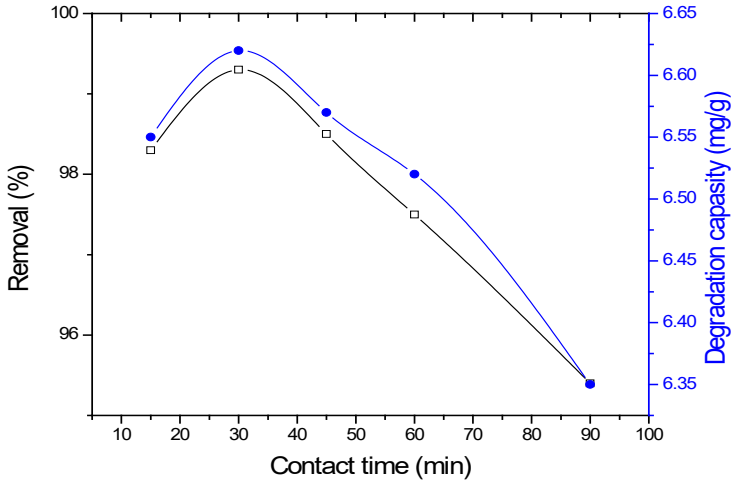

Fig. 8. Effect of contact time on the degeadation of CR by Mn-doped ZnO; dose: 0.6 g/L; concentration: 4 ppm; pH: 7.0; temperature: 30^0C; agitation speed: 150 rpm.

catalyst dose, initial concentration of dye is 77.92 min, 0.6 gl^{-1} and 4mg/l, respectively. (Present experiment also nicely explained the kinetics of dye degradation by using various kinetic equation such as pseudo first order and pseudo second order [e.g. 6,7] and the entire results of the kinetic study are presided in Table 5).

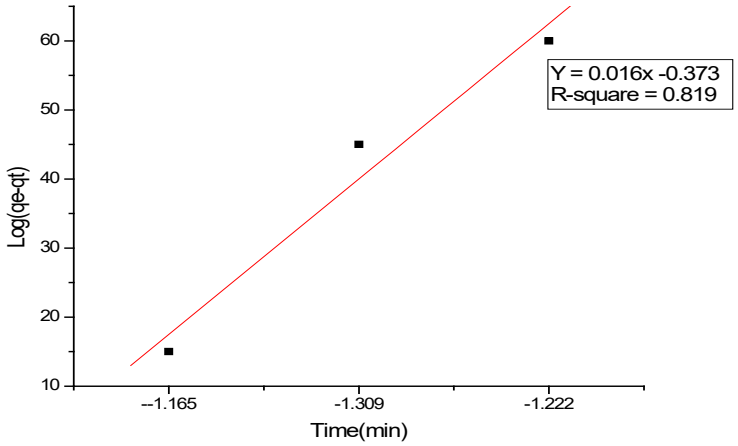

Fig. 9. Pseudo-first-order kinetics for degradation of Congo Red by photocatalytic agent MDZO

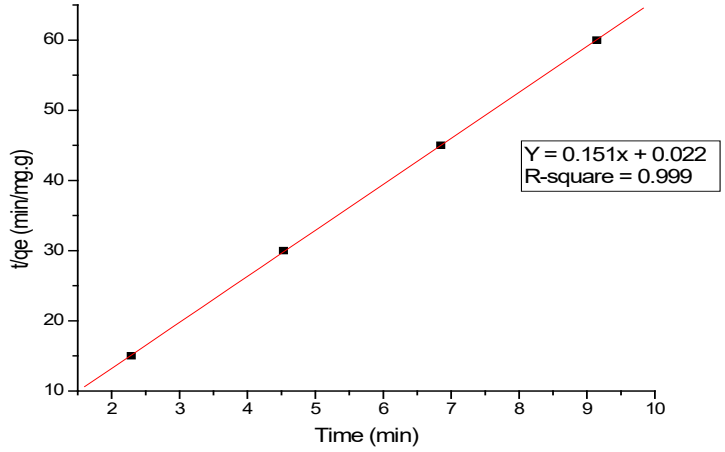

Fig. 10. Pseudo-second-order kinetics for degradation of Congo red by photocatalytic agent MDZO

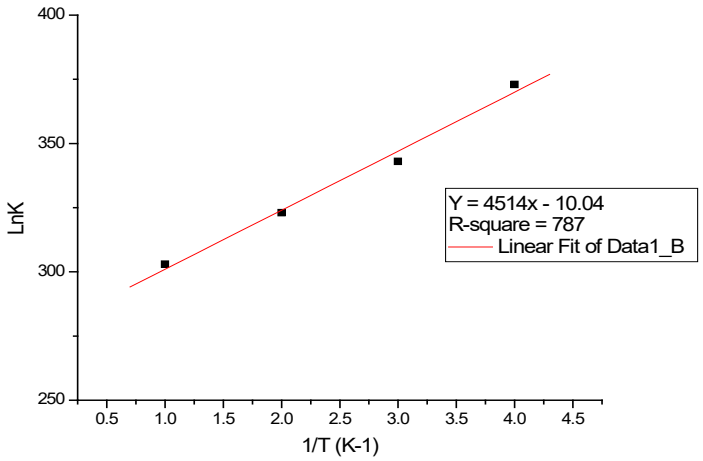

Fig. 11. plot of lnK versus 1/T for the degradation of CR on MDZO

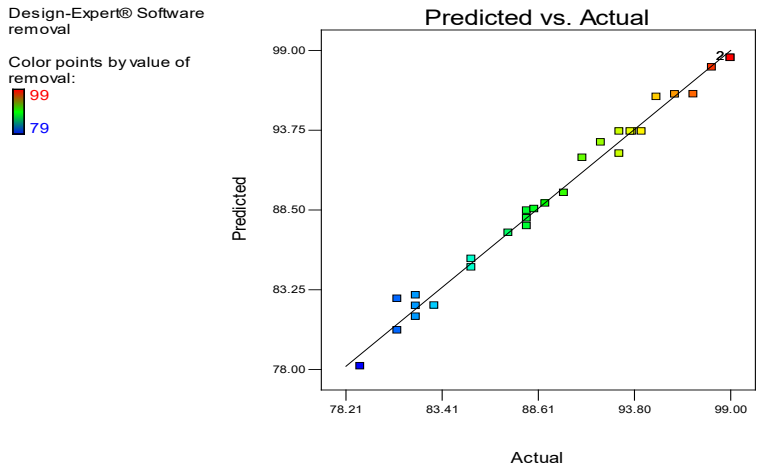

Fig. 12. The actual vs predicted values of photodegradation.

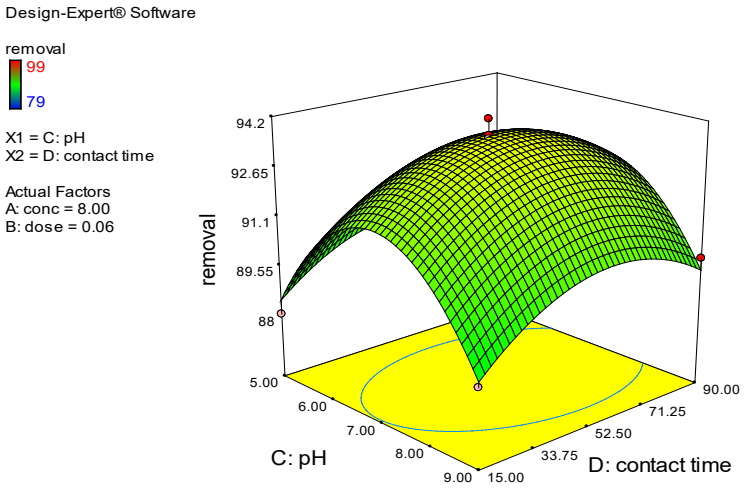

Fig. 13. Interaction between pH and Contact time while holding the concentration at 4 ppm and dose at 0.6 g/L.

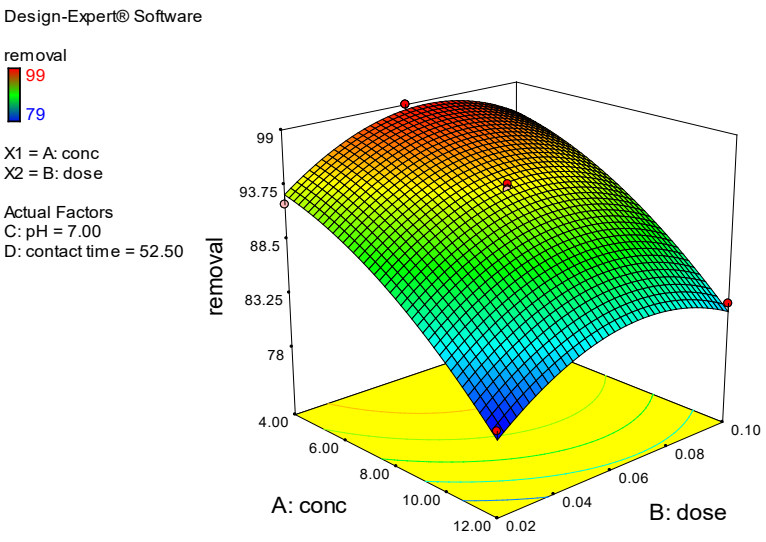

Fig. 14. Interaction between CR concentration and Photocatalyst dose while holding the contact time at 52.50 min and pH at 7.

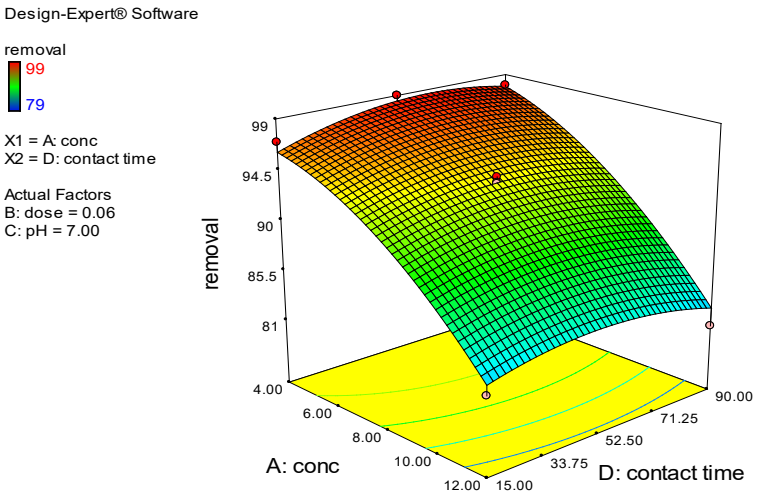

Fig. 15. Interaction between CR concentration and Contact time while holding the dose at 0.6 g/L and pH at 7.

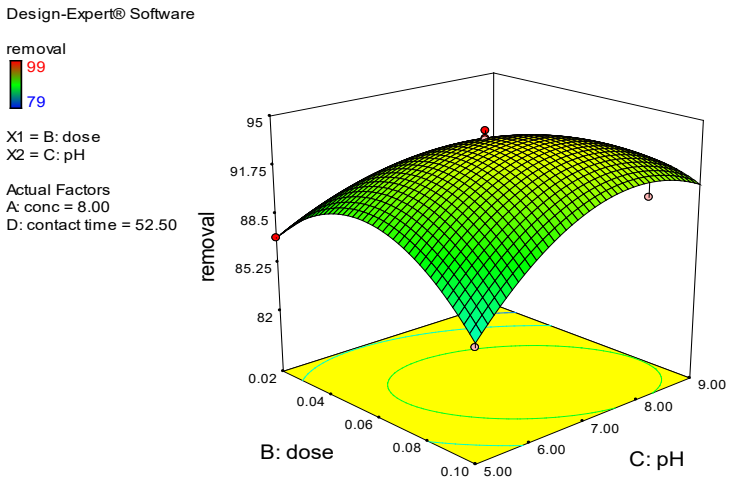

Fig. 16. Interaction between dose and pH while holding the concentration at 4 ppm and contact time at 52.50 min.

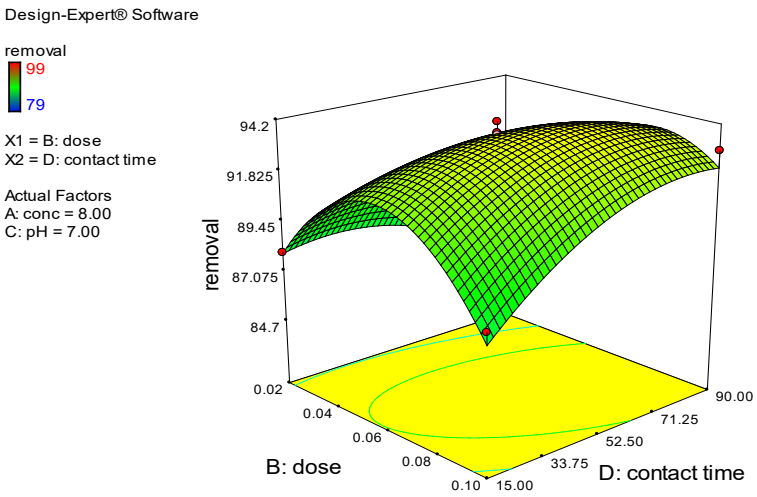

Fig. 17. Interaction between contact time and photocatalyst dose while holding the concentration at 4 ppm and pH at 7.

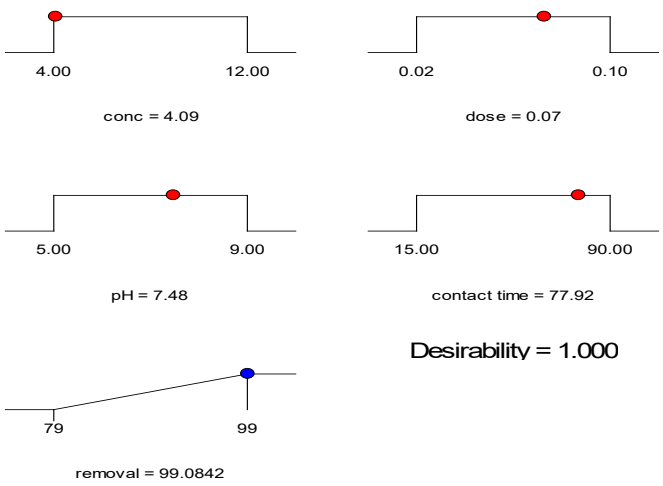

Fig. 18. Desirability function.

Thermodynamic study

Similarly the thermodynamic parameters (ΔG, ΔH and ΔS) of the degradation of CR on MDZO were calculated using equations $\Delta G = -RT \ln K_0$, where R is the ideal gas constant, T is the temperature (K) and K_0 is the distribution coefficient calculated from the experiment. The values of ΔH and ΔS were calculated from the slope and intercept of the Van'thoff plots (Fig. 3c) and listed in Table 6. The negative values of free energy indicate the feasibility of the process and its spontaneous nature (Table 6). The experimental values of at different temperatures are negative. The negative values of for all the systems confirm the exothermic nature of the process. The negative value of ΔS observed for the degradation of CR molecule suggested decreased the randomness during the progress of the process. The thermodynamic values of parameters for the CR reported in the present study and in good agreement with previous research findings (Vijayakumar et al., 2013; Achmad et al., 2012).

CONCLUSION

In this study, manganese was doped in ZnO and its efficacy was assessed towards degradation of azo dye with UV exposure. The results revealed that the degradation efficiency very near to 100% at optimized condition using MDZO photo catalyst. In the sense of adsorption capacity, the improvement of surface structure and porosity of pure ZnO can be done by the incorporation of Mn into ZnO crystal. As results, the enhanced photocatalytic nature of MDZO has sufficient adsorption sites which have more adsorptive attraction with model adsorbate. The degradation data of CR is nicely fitted with pseudo second-order and it is exothermic and spontaneous in nature. ANOVA results suggest that CR dye degradation strongly influenced by catalyst and pH of the medium. On the other hand, the quadratic model depicts that adjusted determination of coefficient and signal to noise ratio are 0.977 and 31.31, respectively. Therefore, it can be suggested that the application of statistical model is an effective approach for optimization, modeling and designing the CR removal process. So this experiment can be considered as a high removal efficiency and regeneracy of Mn-doped ZnO would help in further up scaling decontamination process in agricultural and industries purpose. Finally, the enhancement of high adsorption capacity will be further achievement through different modification of doping treatment.

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CONFLICT OF INTEREST

None.

AUTHORS' CONTRIBUTION

T. K. Roy: conduct the experiment and typing the MS; **P. Mitra**: characterized the Mn-doppedZnO and MS checking; **N. K. Mondal**: Designing the experiment, drafting the MS and overall supervision

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