Photocatalytic Removal of Alizarin Yellow R from Water using Modified Zinc Oxide Catalyst

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The research described about the photocatalytic efficiency of zinc oxide on the photolysis of Alizarin Yellow R. Alizarin Yellow R was used as a model of azo dyes which regarded as a main water pollutants. Some variables influencing the process where studied such as: calcination temperature of catalyst, concentration of the dye, weight of catalyst, time of irradiation and doping by transition metal ions. The best degradation percentage obtained was 92.541 % by using zinc oxide prepared at calcination temperature 773 K, weight 0.3 g, dye concentration 40 ppm and through 2 h irradiation time of dye solution in the presence of medium pressure mercury lamp 400 watt. The percentage obtained was 90.850 % by using ZnO-Co, The kinetic studies showed that the reaction from pseudo first order.

Keywords: Alizarin Yellow R, ZnO, Advanced oxidation process, Modification of catalyst surface.

INTRODUCTION

The pollution is defined as entrance foreign components - whether chemical or physical - to the ecosystem, or biotic side effects of industrial activities leads to direct human damage by water and agricultural products or any type of existing organisms [1]. Pollution can be classified into many types as: air pollution, water pollution or soil pollution. It occurs by harmful inorganic and organic substances or by increasing or decreasing the levels of some main components from natural levels, or by enter new elements to system which they did not originally existed and this gets it from some human activities such as industrial processes, urban constructions and burn fuel in transportation and other. It can also occur as a result of natural disasters as volcanoes and cyclones [2].

Water pollution is physical and biological changes occur in water leading to changes in colour, taste, smell, pH and density which causes a damage in the health and environ-ment [1,3]. Pesticides, industrial dyes, heavy metals and toxic ions (*e.g.*, lead, cadmium, chromium, copper, mercury and zinc) are some examples of water pollutants which are a risk to human health in some industrial effluents. Pollution caused by dyes regards the main source of environmental pollution that lead to the undesirable situation not only because of their colours, but because so many toxic decomposed products such as polychlorinated naphthalenes and benzidine that are causing cancer [4,5].

Azo dyes are the important type that containing azo group with double bonds (-N=N-) causing of high stability of the dyes and form more than half of the dyes used in the present time [6]. Alizarin Yellow R is one of the types of azo dyes and also called alizarin yellow sodium salt or 5-(*m*-nitrophenylazo) salicylic acid sodium salt, which have the structural formula as illustrated in Fig. 1. It discovered by Rudolf Nietzki 1887 where produce from the dialysis of *m*-nitroaniline and associate with salicylic acid [7]. It is used as a reagent for acidity and for dyeing wool and other fibers like silk and nylon. There are three methods used to treat water pollution *viz.*, physical, bio-logical and chemical methods [8].
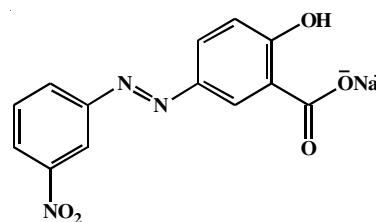

Fig. 1. Structural formula of Alizarin Yellow R

Advanced oxidation processes is of chemical methods and indicate the range of processing techniques designed to remove organic and inorganic substances in water and wastewater by oxidation [9]. These methods include generating effective free radicals such as hydroxyl radicals $HO^\bullet$. It can be classified into two groups: homogeneous methods which including non-photo reactions as: (O_3, H_2O_2, $O_3/H_2O_2/Fe^{2+}$ (Fenton system), $O_3/H_2O_2/cat$, US, O_3/US) and photo reactions as (O_3/UV, H_2O_2/UV, $H_2O_2/O_3/UV$, $H_2O_2/Fe^{2+}/UV$ (Photo-Fenton), UV/TiO_2,

TiO$_2$/UV/H$_2$O$_2$, O$_2$/TiO$_2$/UV, UV/US). The second group is heterogeneous methods (Heterogeneous photocatalysis: ZnO/UV, SnO$_2$/UV, TiO$_2$/UV, H$_2$O$_2$/UV/TiO$_2$) [8-10].

This paper aimed to study the effect of modification of zinc oxide surface such as sintering and doping with transition metal ions - onto catalyst photo activity toward reaction of Alizarin Yellow R and effect dye concentration and weight of zinc oxide. The physical properties of the catalyst such as surface area and porosity were determined.

EXPERIMENTAL

Alizarin Yellow R was obtained from Merck, zinc chloride was supplied from SDFCL. Absolute ethanol was obtained from ScharlauChemie SA, Copper nitrate trihydrate, nickel chloride and cobltous chloride were from BDH.

UV-visible spectrophotometer UV-1650 (Shimadzu, Japan) used to recording the absorption spectra of aqueous solutions of dye and IR spectrophotometer FTIR 8000 Series and X-ray diffractometer LabX XRD- 6000 (Shimadzu, Japan), surface area analyzer SA-9600 (HORIBA Scientific, USA), Photo Reactor Immersion type -3210 (SAIC, Chennai, India) using medium pressure mercury lamp 400 watt.

Photo reactor: The photoreactor was cylindrical in shape with 1 L volume and made from glass which was available for the transfer of the radiation. Irradiation was achieved by using UV lamp medium pressure mercury lamp (MPML) which was immersed in the glass tube. The UV lamp was equipped with a cooling water space which placed in the reactor vessel. The reaction chamber filled with the reaction mixture, which placed between the reactor walls and UV lamp system.The reactor placed onto magnetic stirrer hot plate to make the homogeneous mixing.The reaction was supplied with oxygen by using oxygen bubbler. The temperature of photoreaction was controlled at 303 K for all experiments using thermosetting circulating water bath. Samples of dye were irradiated at a period of time and then centrifuged by centrifuge. Finally the absorbance was taken by UV-visible spectrophotometer

Preparation of zinc oxide: Zinc oxide was prepared by precipitation method as the following procedure. 32000 ppm solution of sodium hydroxide was added drop by drop to 54400 ppm solution of zinc chloride through 20 min with continuous stirring for 2 h. Then filtered and washed many times with deionized water dried in oven for 1 h to be calcined at (673, 773, 873, 973) K.

Preparation of calibration curve: 500 ppm stock solution was prepared by dissolving 0.5 g of dye in 1000 mL distilled water as a solvent. Other solutions were prepared from stock solution in the range (5-50 ppm). λ_{max} was specified at 353 nm using a UV-visible spectrometer.

Effect of calcination temperature: 0.3 g of ZnO calcined at different temperatures was added to 30 ppm of Alizarin Yellow R dye solution and exposure to ultraviolet light through 120 min with constant stirring in the presence of oxygen. The irradiated samples were taken every 15 min and the absorbance was measured at 353 nm.

Effect of dye concentration: 0.3 g of ZnO calcined at 773 K was added to different concentrations of Alizarin Yellow R dye ranging (30, 40, 50, 60) ppm. The solution was exposure

to ultraviolet irradiation through 120 min in the presence of oxygen. Then the irradiated samples were taken every 15 min and the absorbance was measured at 353 nm.

Effect of catalyst loading: The study of the effect of catalyst loading was done using different weights of catalyst ranging (0.05, 0.1, 0.3, 0.5, 0.7) g which were calcined at 773 K. 40 ppm of Alizarin Yellow R was exposed to ultraviolet irradiation through 120 min in the presence of oxygen. Then the irradiated samples were taken every 15 min and the absorbance was measured at 353 nm.

Effect of metal ions doping: Impregnation method was used to study the effect doping with metal ions on the photo activity of catalyst. Appropriate amounts (1 % w/w) of copper nitrate trihydrate, cobaltous chloride and nickel chloride -which were used as a sources of ions Cu^{2+}, Co^{2+} and Ni^{2+} respectively-added to 100 mL of distilled water with 0.3 g of ZnO. The mixture stirred continuously overnight. Then the precipitates were dried, washed with distilled water and heated at 673 K. 0.3 g from doped ZnO was added to 40 ppm of Alizarin Yellow R and exposure to ultraviolet irradiation through 120 min in the presence of oxygen. Then the irradiated samples were taken every 15 min and the absorbance was measured at 353 nm.

The percentage of conversion in all experiments was estimated as the following equation:

$$\text{Conversion \%} = \frac{C_o - C}{C_o} \times 100 \qquad (1)$$

where C_o is the initial concentration of dye and C is the concentration of dye after irradiation.

RESULTS AND DISCUSSION

X-ray diffraction: X-ray diffraction technique was used to study the crystallization of the prepared catalyst at different calcination temperatures (673, 773, 873, 973) K through 1 h (Fig. 2). It is noted that the peaks correspond to the hexagonal (wurtzite) of zinc oxide (JCPDS Card, No. 36-1451) [11].
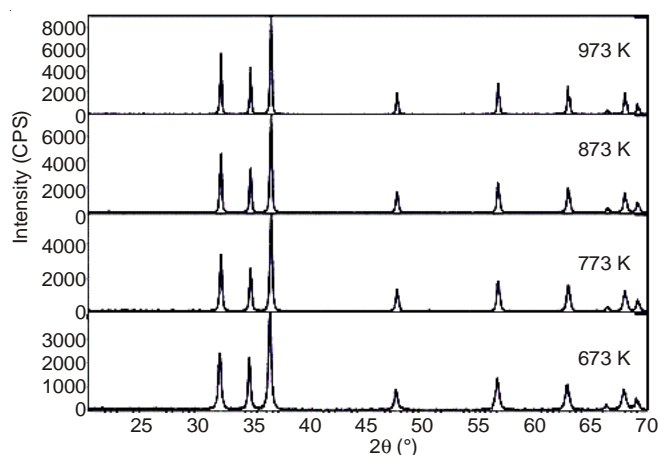

Fig. 2. XRD of ZnO at different calcination temperatures

The intensity of the peaks increases with increasing of calcination temperature so as to increasing of crystalline size. In high temperatures, migration causing accumulation the small grains to yield large grains [12].

The average crystalline size of the calcined ZnO powder is estimated by the Scherrer's relation (2).

$$D = K\lambda/\beta_{1/2}\cos\theta \qquad (2)$$

where D is the average crystalline size, K is Scherrer's constant (0.9), λ is the X-ray wavelength of 1.54 Å, θ is the Bragg diffraction angle and $\beta_{1/2}$ is the FWHM [13]. The morphology constants of the higher peak were described in Table-1.

Infrared spectra of prepared ZnO: Infrared spectra were recorded within the range (4000-400) cm^{-1} using KBr discs. The appearance of broad band of IR spectrum at 3400 cm^{-1} belongs to stretching vibration peak of hydroxyl group which its intensity decreases at higher temperatures and an absorption peak was appeared at 1625 cm^{-1} which belongs to bending vibration peak of hydroxyl group. In addition to that, an absorption peak was appeared at 501-401 cm^{-1} which belongs to stretching vibration peak of ZnO [14] (Fig. 3).
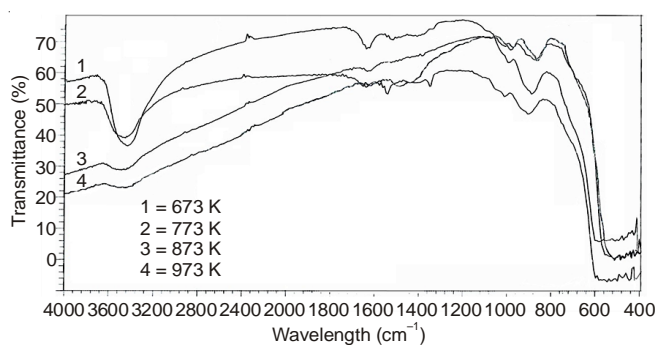

Fig. 3. FT-IR spectra of ZnO at different calcination temperatures

Electronic spectra: UV spectra of the prepared ZnO was measured at different calcination temperatures (673, 773, 873, 973) K by dissolved 0.1g of ZnO in 10 mL absolute ethanol. An absorption peak was appeared at 378 nm [15], which belongs to absorption band band-gap of ZnO because of the electron transition from valence band to conduction band(O 2P→Zn 3d) [11] (Fig. 4).

Fig. 5 represented the electronic spectrum of dye that found the limits of wavelength 353 nm for azo groups N=N which belongs of transitions n→π* [16,17].

Calibration curve: The calibration curve showed the linear relation between absorbance and concentration which obeyed Beer-Lambert law in concentration range (5-50 ppm) if concentration high the range the calibration curve deflects and not obeyed Beer-Lambert law, calibration curve showed in Fig. 6.

Adsorption study: The time of adsorption-desorption was examined in the dark using 30 ppm of dye, 0.3 g of ZnO and pH = 8. It was be found that the percent of residual concentration of Alizarin Yellow R decreased as time increased. This
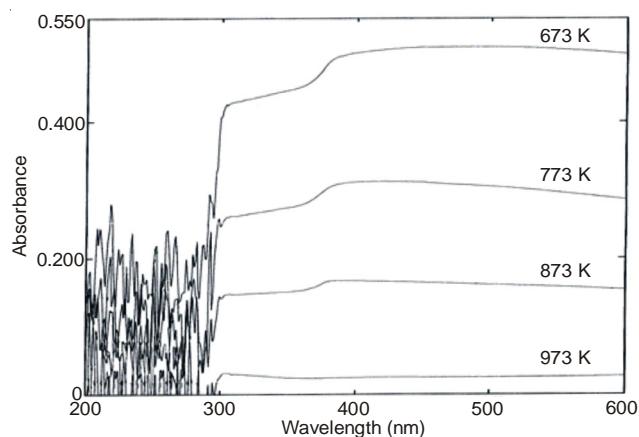

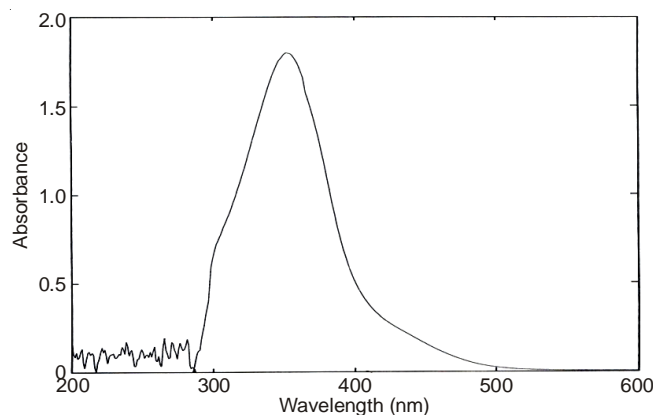Fig. 4. Electronic spectra of ZnO at different calcination temperatures

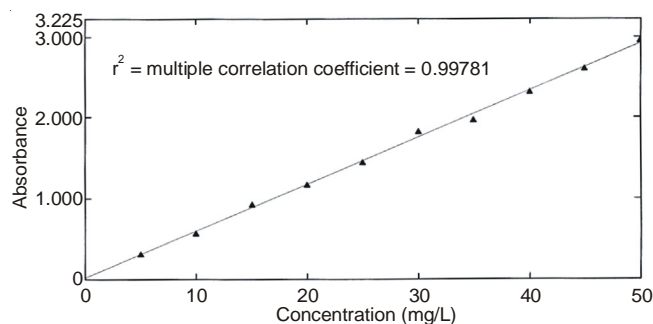Fig. 5. Electronic spectrum of Alizarin Yellow R dye

Fig. 6. Calibration curve of Alizarin Yellow R dye

can be explained due to abundant vacant active sites onto catalyst surface which had the capability to bind with dye. The numbers of active sites been high at the primary process of adsorption then they will be filled through the time as a result their numbers will be decrease at constant value until reach to the equilibrium state [18]. The equilibrium time was chosen as 0.5 h (Fig. 7).

Effect of the calcination temperature on surface area and porosity of zinc oxide: The effect of calcination temperature in the surface area and porosity of the catalyst was

| Calcinations temperature (K)	d-Value (Å)	FWHM	Crystallite size (D) (nm)	Lattice strain (nm)	Unit cell parameters (Å)		c/a ratio	Cell volume (Å)^3
					a	c		
663	2.4772	0.2945	29.7618	0.4426	3.2511	5.2058	1.6012	47.6503
773	2.4699	0.2376	36.9007	0.3559	3.2407	5.2017	1.6051	47.3100
873	2.4704	0.2113	41.4927	0.3165	3.2414	5.2029	1.6052	47.3397
973	2.4701	0.1685	52.0347	0.2524	3.2408	5.2022	1.6052	47.3156

TABLE-1
MORPHOLOGY CONSTANTS
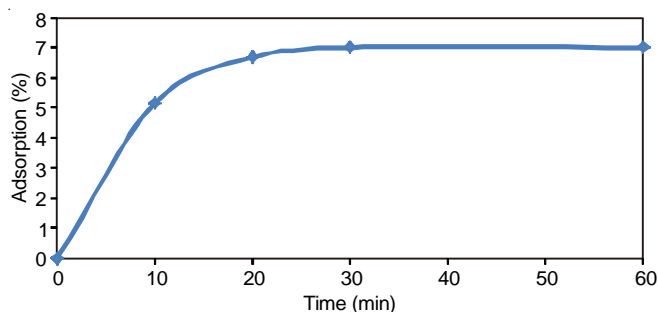
Fig. 7.   Relation between percentage of adsorption of Alizarin Yellow R dye and the time of equilibrium [conc. = 30 ppm, solvent = water, ZnO = 0.3 g, pH = 8, temp. = 298 K]

studied at different temperatures (673, 773, 873, 973) K. The surface area was estimated using the method of BET [19]. Both surface area and porosity have maximum value at 773 K then decrease with increasing temperature which is due to the decreasing in crystalline size due to shrinkage in surface area [20] (Table-2).

TABLE-2
SURFACE AREA AND POROSITY OF ZnO
AT DIFFERENT TEMPERATURES

Calcination temperature (K)	Surface area (m²/g)	Porosity (%)
663	7.5253	79.2407
773	8.222	83.8454
873	4.2045	80.4852
973	2.3049	78.8869

Effect of irradiation time: Fig. 8 shows the effect of irradiation time on the removal efficiency of the dye. It can be seen that the conversion of a small part of the dye increases when the irradiation time increases. This is due to the increase of excited zinc oxide particles with the time and thus increase the number of produce HO• radicals and positive holes [21].
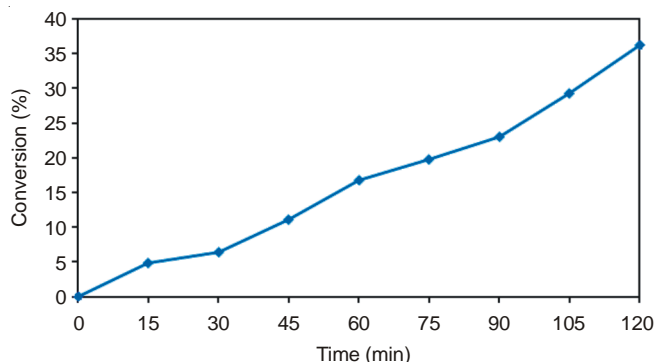

Fig. 8.   Effect of irradiation time on the removal efficiency of Alizarin Yellow R dye [conc. = 30 ppm, solvent = water, pH = 8, temp. = 298 K]

Effect of calcination temperature on the photoactivity of ZnO: The study showed that high photoactivity of catalyst at 773 K due to higher surface area, as a result the percent of conversion of dye was a higher value at 773 K (Fig. 9).

Effect of dye concentration: The results indicated that the higher value of removal percent of dye was at low concentrations because to provide enough surface for adsorption, in
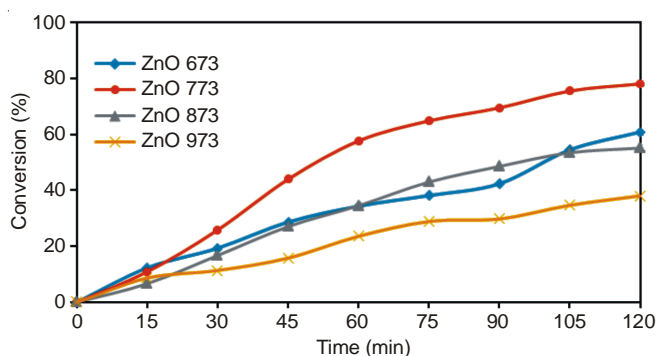

Fig. 9.   Effect calcination temperatures on the removal efficiency of Alizarin Yellow R dye [conc. = 30 ppm, solvent = water, ZnO = 0.3 g, pH = 8, temp. = 298 K]

addition to formation of hydroxyl radicals in the solution [22]. The decolourization decreased with increasing dye concentration because the higher concentrations of dye reduces the penetration of ultraviolet irradiation into the solution and reduces number of hydroxyl radicals [23,24]. The optimum concentration of dye was 40 ppm (Fig. 10).
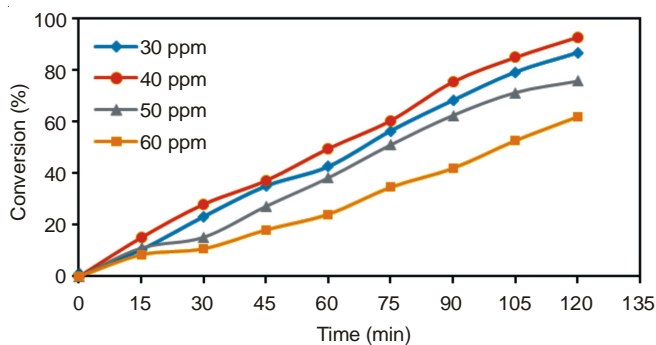

Fig. 10. Effect of dye concentration on the removal efficiency [solvent = water, ZnO = 0.3 g, pH = 8, temp. = 298 K]

Effect of catalyst loading: The results indicated that the percentage of dye removal increased with increasing weight of adsorbent. The increase in weight of adsorbent means increasing the number of active sites formatted to adsorption of the dye on the surface so the percentage increases until it reaches a specific value represents the amount of adsorbent in the saturation stage and then decreased the amount of adsorption increased weight [25]. This is due to the adsorption process that requires initially a balance between adsorbent and the adsorbate to occupy all the active sites of the material adsorbent which makes the adsorption process is stable on the surface and reach the amount of adsorption to the highest value, but that the increase in weight of catalyst then may lead to the spread of unstable of catalyst surface large compared to the amount of the adsorbent [26].

Thus the energy of adsorbate solvation will overcome on the energy of adsorption leading to the decreasing of adsorbate on catalyst surface. As well as the increase in the weight of ZnO causes an increase in turbidity of solution leading to a decrease in penetrating ultraviolet radiation due to increased blocking light by the catalyst suspended in the solution molecules [27]. It was found that the best weight was 0.3 g, which gave the highest percentage of decolourization (Fig. 11).
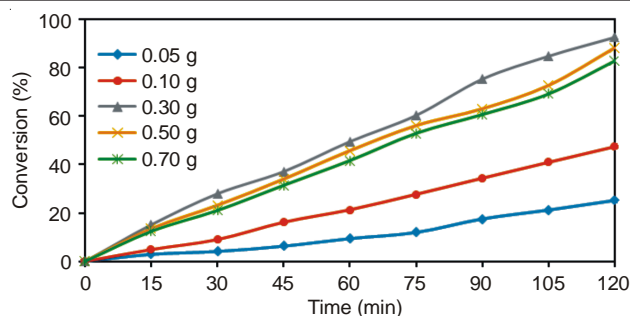
Fig. 11. Effect of catalyst weight on removal efficiency of Alizarin Yellow R dye [conc. = 40 ppm, solvent = water, pH = 8, temp. = 298 K]

Effect of doping with transition metals ions: Doping of zinc oxide with transition metal ions was studied. The use of metal ions allows transmission electron trap that suppress electrons holes recombination. The electron is then able to migrate toward the surface of the catalyst and oxidizes the adsorbed dye [28]. The Zn^{2+} ions are replaced by M^{2+} ions, metal ions exist in a tetrahedral crystal field in the +2 state without destroying the Wurzite crystal structure of ZnO [29,30]. The undoped ZnO more photocatalytically active compared to the doped (Co, Ni, Cu) (Fig. 12).
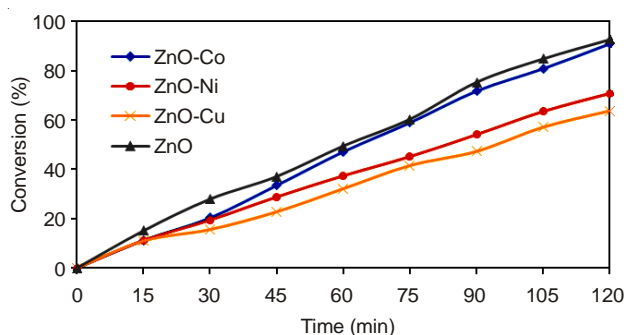

Fig. 12. Effect of doping on removal efficiency of Alizarin Yellow R dye [conc. = 40 ppm, solvent = water, pH = 8, temp. = 298 K]

The kinetics of photodegradation reaction expressed the pseudo first order reaction. The rate constants are shown in Table-3.

TABLE-3
VALUES OF RATE CONSTANTS OF PHOTOLYSIS OF ALIZARIN YELLOW R AT DIFFERENT CONDITIONS

Factor		Rate constant (k) × 10^{-2} (min^{-1})
Calcination temperature (K)	673	0.8
	773	1.1
	873	0.7
	973	0.3
Concentration (ppm)	30	1.3
	40	1.9
	50	1.1
	60	0.8
Weight (g)	0.05	0.2
	0.10	0.5
	0.30	1.9
	0.50	1.8
	0.70	1.4
Doping	Cu	0.8
	Ni	1.0
	Co	1.7

Conclusion

The photo reaction showed that the dye removal efficiency increased with increasing irradiation time. The kinetics of photodegradation reaction expressed the pseudo first order reaction. The increasing of dye concentration decreased dye removal efficiency. The optimum catalyst weight was 0.3 g while the optimum concentration of dye was 40 ppm. The higher removal efficiency was at 773 K calcination temperature. The undoped ZnO was more photocatalytically active as compared with the doped (Co, Ni, Cu). Cobalt doped ZnO was optimum catalyst doping towered Alizarin Yellow R dye removal.

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