Research Article

SOHAG JOURNAL OF SCIENCES

https://doi.org/10.21608/sjsci.2025.355277.1252

Photocatalysis performance for $Cd_xZn_{1-x}Co_2O_4$ spinel oxide

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Received: 24th January 2025, **Revised:** 24th April 2025, **Accepted:** 26th April 2025
Published Online: 23rd May 2025

Abstract: In this study, Photocatalytic performance of $Cd_xZn_{1-x}Co_2O_4$ nanostructured spinel oxides with varying cadmium (Cd) concentrations (x = 0, 0.25, 0.5, 0.75, 1) were studied. Their photocatalytic activities were evaluated by measuring the degradation of methylene blue (MB) under UV- irradiation for different times (0, 10, 20, 30, 40, 50 and 60 min) before and after potential of hydrogen (pH) effect. The results show that $Cd_xZn_{1-x}Co_2O_4$ nanostructured spinel oxides with different Cd-doping (x) verified the photocatalytic capabilities. The degradation efficiency enhanced after pH effect for all samples. The doping x = 0.5 has the highest efficiency for MB degradation before pH effect (33%) and it enhanced after pH effect to reach 88%. Our work will be helpful in the photocatalytic activity of Cd $ZnCo_2O_4$, the photocatalytic degradation of MB under UV light was examined. In order to comprehend their photocatalytic characteristics. Moreover, this work will be useful in the process of photocatalysis affordable and effective way to break down organic pollutants in wastewater.
Keywords: Nanostructure $Cd_xZn_{1-x}Co_2O_4$ spinel oxide, Methylene blue spectra absorption, Degradation efficiency, UV- irradiation time.

1. Introduction

New materials for dye removal are the goal of significant research. Dyes such as crystal violet (CV), rhodamine B (RhB) and methylene blue (MB) are harmful to the environment [1]. To reduce the possibility of industrial wastewater pollution must be adequately treated before it is drained [2]. To break down organic pollutants in wastewater, the photocatalysis process is an effective path [3]. In this field, finding a highly effective, stable, inexpensive and earth-abundant photocatalyst is therefore one of the major challenges.

Lately photocatalysts featuring a spinel type structure have emerged as the most researched candidates because of their affordabilit, excellent reusability, strong photoelectronchemical performance, and stable architecture [4, 5]. Photocatalysis has garnered significant attention due to its potential applications in environmental remediation and renewable energy [6]. Numerous AB_2O_4 spinel structures have been examined as photocatalysts to improve the utilization of the solar spectrum. Among the spinel oxides with catalytic properties is $ZnCo_2O_4$ [7-9]. It demonstrated high catalytic activity for the oxidation of CO + H_2 mixtures [10] and was discovered to be an active electrocatalyst for the O_2 evolution reaction [11]. There are different techniques, such as electrochemical deposition, interfacial polymerization, self-assembly with templates, and electrospinning, has been employed to fabricate nano fibers [12-16]. The photocatalytic performance is related to the specific surface area of the materials, so it is important to find an effective method to immobilize catalyst while keeping high surface to volume ratio realizing the industrial application of the photocatalysis in wastewater disposal and air purification [17].

Spinel oxides with the general formula AB_2O_4, are particularly interesting because of their utility in applications such as catalysis, energy storage, magnetism, optics, and electronics [18]. Among them, $ZnCo_2O_4$ has considerable promise material for efficient dye photocatalytic degradation [19]. Introducing Cd into the $ZnCo_2O_4$ lattice to form $Cd_xZn_{1-x}Co_2O_4$ solid solutions offers a pathway to modulate these properties, potentially enhancing photo catalytic performance. The $ZnCo_2O_4$ sample was prepared using the sol-gel method among various available methods as this method offers several advantages, including high homogeneity, low processing temperature, the ability to produce nanoparticles with high surface area [20].

This study aims to understand how different Cd/Zn ratios influence the photocatalytic properties before and after pH effect of these materials, which are prepared in nanostructure as studied previously with other structure, morphology and optical properties in our previsoly published paper [21].

2. Experimental technique

The photocatalytic performance of $Cd_xZn_{1-x}Co_2O_4$ with x = 0, 0.25, 0.5, 0.75, and 1, in nanostructure samples are studied by measuring the degradation (absorption spectra) of methylene, MB, before and after pH effect under UV-irradiation for different times from 10 min to 60 min. A 40 mg/L of MB solution was used, and 3 mg of the photocatalyst was dispersed in 40 mL of this solution. Prior to irradiation, the suspension was stirred in the dark for one hour to establish adsorption- desorption equilibrium. Ice- water used throw UV-

irradiation to keep the temperature constant until the run end, to eliminate the temperature parameter for MB-degradation process. The samples stirring for 10 minutes in the centrifuge for 3 minutes after exposure for UV- irradiation (as shown in Scheme 1). The absorption of the all the samples measured by double beam spectrophotometer (*Jasco V-570, Japan)* in thewavelength range from 400 to 800 nm.

3. Results and discussion

Light or photon sources are necessary for the photocatalysis process to activate the photocatalyst [22-24]. The primary driving force behind this technique is photon absorption, which produces photo generated electron and hole pairs (e−- h+). The elec trons are excited from the valance band of the catalyst to the conduction band, leaving the holes behind in the valance band. The free electrons react with the oxygen and the hole with the hydroxyl (OH). Eqs. (1- 4) exposure to these reactions and the radicals which degrade the methylene blue [25].

$$Cd_xZn_{1-x}Co_2O_4 + UV \rightarrow Cd_xZn_{1-x}Co_2O_4\ (e^- + h^+) \quad (1)$$

$$O_2 + e^- \rightarrow O_2^{\bullet -} \quad (2)$$

$$OH^- + h^+ \rightarrow OH^{\bullet +} \quad (3)$$

The hydroxyl radical that comes from the oxidation of adsorbed water or the absorbed OH^- is the main oxidizer in the decomposition of organic compounds methylene blue (MB). The presence of oxygen prevents the re-combination of hole-electron pairs due to the reduction process as the oxygen traps the free electrons, so the holes have not the chance for recombin with free electrons which allow it to produce hydroxyl radicals and also increase the photo catalytic activity [26]. The final products for a complete reaction are carbon dioxide and water among others [27, 28]:

$$^{\bullet}OH + h^+ + MB \rightarrow CO^2 + H_2O + NH_4^+ + Cl^- + NO_3^- + SO_4^{2} \quad (4)$$

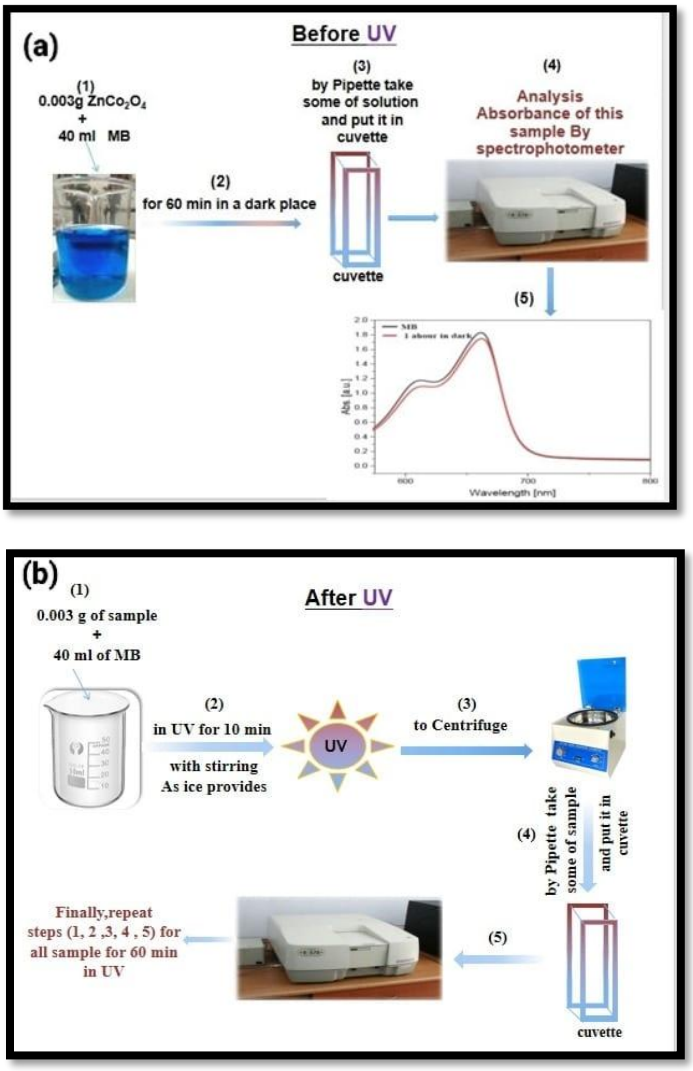
The decomposition rates of reaction follow pseudo-first-order kinetics according to the Langmuir-Hinshelwood (L-H) model, so the rate of the reaction constant (*K*), the degradation efficiency (η) and half time ($t_{1/2}$) can be calculated by the following equations [28-33]:

$$\frac{C_t}{C_o} = e^{-Kt},\ -\ln\frac{C_t}{C_0} = Kt \quad (5)$$

$$\eta = \frac{A_0 - A_t}{A_0} \times 100 = \frac{C_0 - C_t}{c_0} \times 100 \quad (6)$$

$$t_{1/2} = \frac{\ln(2)}{K} \quad (7)$$

Where A_0, A_t and C_0, C_t are the absorbance of MB and the MB concentration (mg/L) when the irradiation time is 0 and *t*, respectively. *K* is the decomposition rate constant of the reaction. $t_{1/2}$ is the half lifetime for half MB degradation. Fig. 1 shows the absorption spectra of $Cd_xZn_{1-x}Co_2O_4$ ($0 \le x \le 1$) powdered samples in MB before and after UV irradiation. The absorption peak for all the samples is shown in Fig.1 appears at 662 nm which means that light irradiation did not shift the peak [29]. From Fig. 1, the effect of UV-irradiation time is noticed clearly on the absorption process of the sample with x=0 and enhanced continuously until x=0.5 then this effect decreases reaching to x=1.



Scheme 1: The absorption measurement (a) before pH and (b) after pH.

Figure 2 shows the relation of ln (C_t/C_0) with time and the efficiency η with time for $Cd_xZn_{1-x}Co_2O_4$ ($0 \le x \le 1$) powder samples which were calculated from the Eqs. (1, 2). It is obvious from Fig. 2a that ln (C_t/C_0) with time, shows an invers behavior for η with time for all the irradiated samples (Fig. 2b). The efficiency η for all the samplesas shown in Fig.2b increases with increasing irradiation time and reaches saturation nearly from 30 to 60 minutes, except the $Cd_{0.5}Zn_{0.5}Co_2O_4$ ratio which has a contentious increasing behavior with increasing UV- irradiation time reaching the value of 60 min.This indicates thatthe $Cd_{0.5}Zn_{0.5}Co_2O_4$ ratio has thehighest photocatalytic activity.The efficiency reached the valueof 33% after 60 min. UV-irradiation and this value is the highest value for the selected *x*-ratio (Table 1). This result agrees well with the the results of the absorption spectra plotted in Fig. 1.

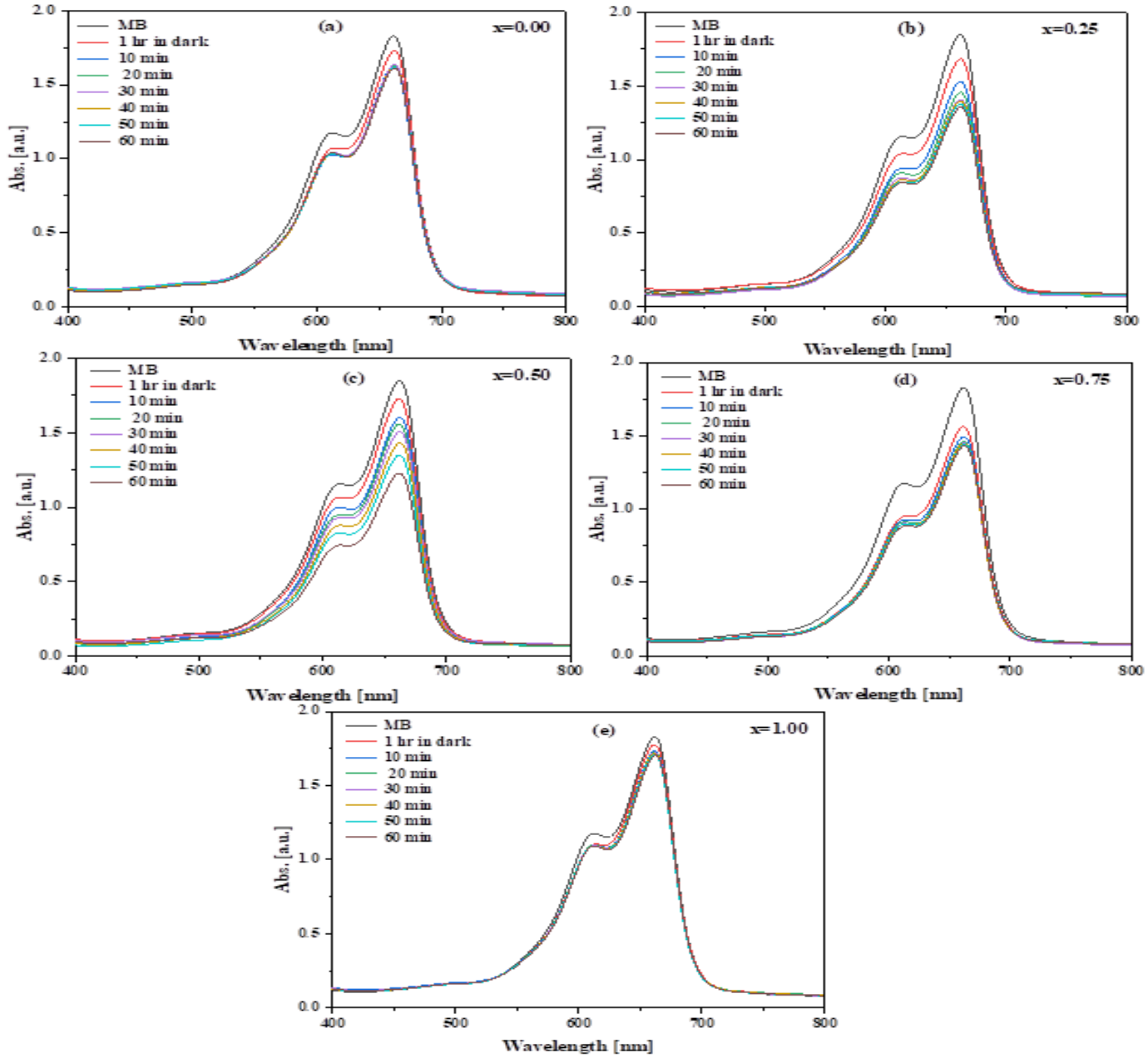


Figure 1: (a-e):The absorption spectra of $Cd_xZn_{1-x}Co_2O_4$(x=0, 0.25, 0.5, 0.75, 1) powdered samples in MB before and after different times UV irradiation.

The degradation of pollutants is affected by different parameters such as specific surface areas (SSA) of samples, morphology, and the width of the band gap [35]. The SSA, the morphology and the optical properties of $Cd_xZn_{1-x}Co_2O_4$spinel oxide was studied in our previsoly published paper [21], which recorded the decreasing in optical band gap by increasing Cd-doping ratio (x) and the highest value for SSA was found to be 75.8 m^2 g^{-1} recorded for the ratio of x=0.5. This high SSAvalue is responsible for the highest value of photocatalytic activity for $Cd_{0.5}Zn_{0.5}Co_2O_4$ spinel oxide ratio [36], despite its optical band gap is not the lowest value between the selected Cd-doping values.

To enhance the degradation efficiency, potential of hydrogen (pH) effect should be studied as it increases the reaction between the radicals and the organic pollutant MB. Different values from acidic to basic conditions (pH=2,6,10,13) tested in MB with$Cd_{0.5}Zn_{0.5}Co_2O_4$ compound as shown in Fig. 3. The basic condition is thatpH=13 has the lowest absorption spectra for all the samples studied. The absorption spectrum was plotted for the ratio of x=0.5 with pH=13 at different UV irradiation times in Fig. 4, which presents a decrease in the value of the absorption spectra. The values of ln (C_t/C_0) and the degradation efficiency are calculated and plotted with UV-irradiation time in Fig. 5. Which shows that the lowest value of ln (C_t/C_0) and also the highest value of degradation efficiency for $Cd_{0.5}Zn_{0.5}Co_2O_4$ spinel oxide (x=0.5). The efficiency reached the value of 88%

after 60 min irradiation time. In the other side the *K* values are calculated from the slope of the relation of Eq. (2). There sulting values are recorded in Table 1. It is obvious that all *K* values were increased, and $t_{1/2}$ values decreased after pH effect for all the samples studied.

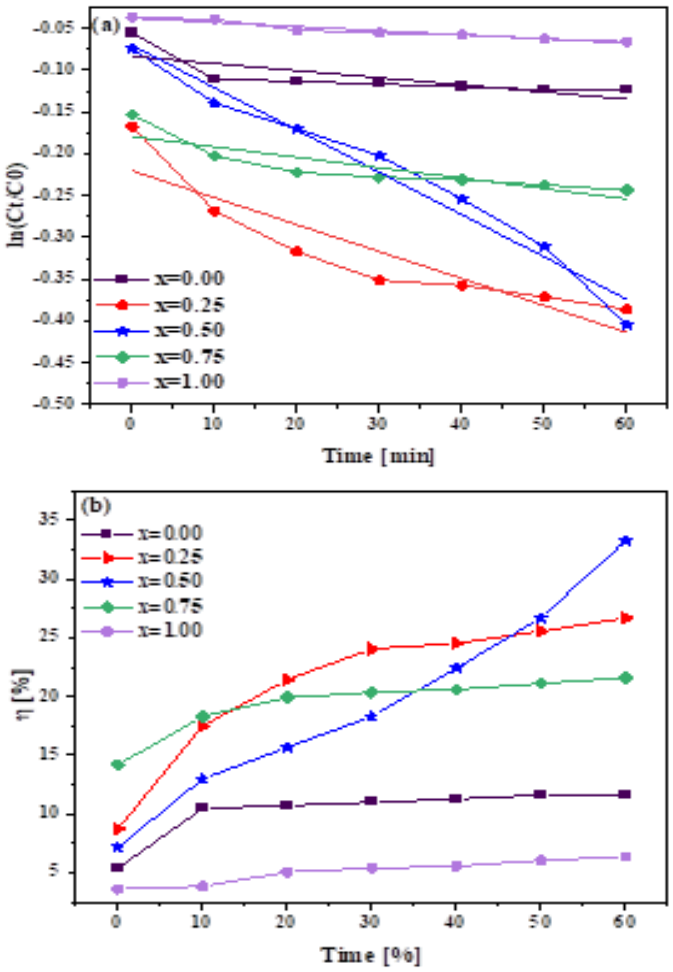


Figure 2: The relation of ln (C_t/C_0) with time (a) and η with time (b) for $Cd_xZn_{1-x}Co_2O_4$ ($0 \le x \le 1$) powdered samples.

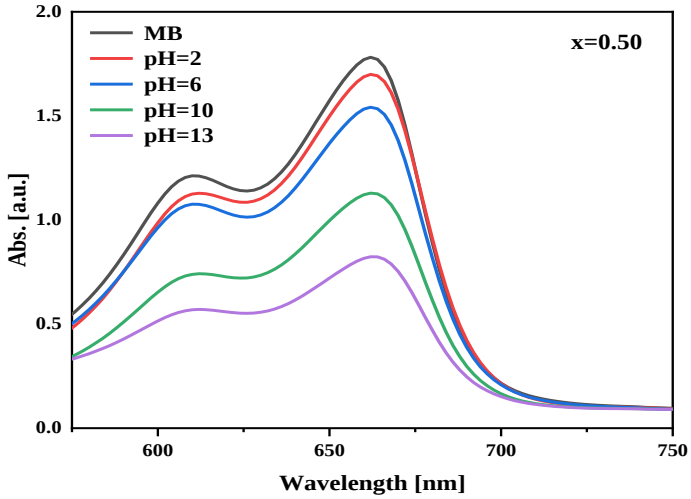


Figure 3: The absorption spectra of $Cd_{0.5}Zn_{0.5}Co_2O_4$powdered sample in different pH values.

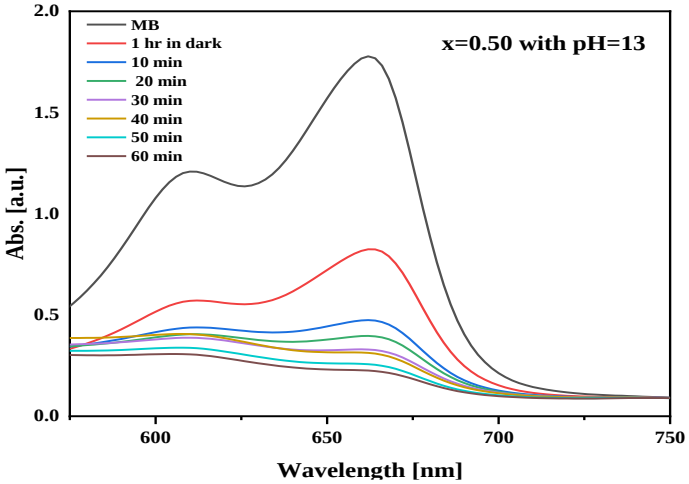


Figure 4: The absorption spectra of $Cd_{0.5}Zn_{0.5}Co_2O_4$powdered sample with pH=13 at different irradiation times.

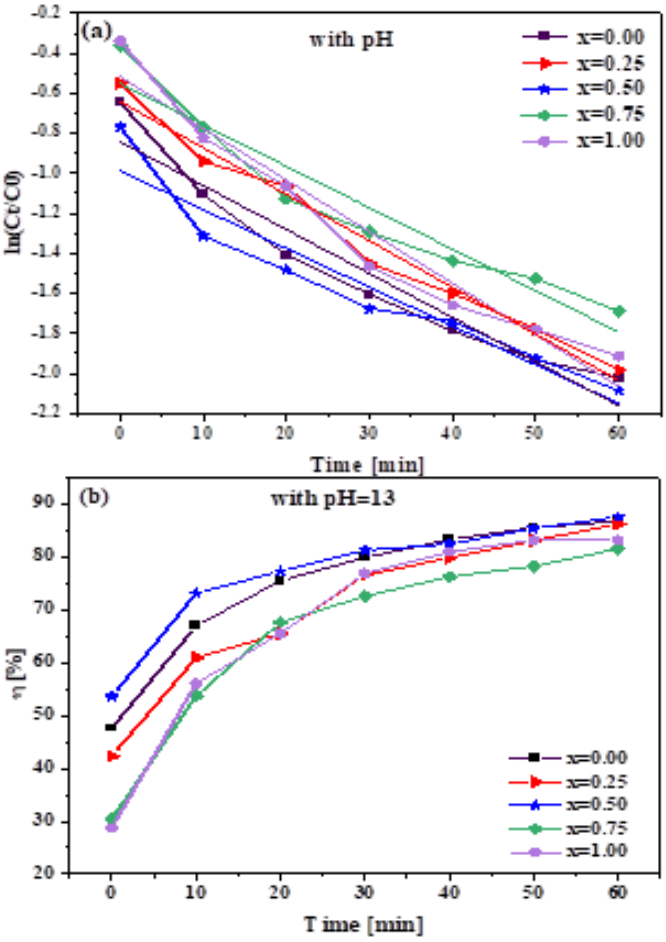


Figure 5:The relation of ln (C_t/C_0) with time (a) and η with time (b) for $Cd_xZn_{1-x}Co_2O_4$ ($0 \le x \le 1$) powdered samples with pH =13.

4. Conclusions

PhotocatalysisperformanceforCdxZn1xCo2O4spinelnanostructured oxides with varying Cd concentrations (x = 0, 0.25, 0.5, 0.75, 1) were studied. The degradation efficiency and $t_{1/2}$ for all samples before and after the pH effect with UV- iradiation for different times (10,20,30,40,50, 60 min) are studied. The results show that $Cd_xZn_{1-x}Co_2O_4$spinel oxides prepared in

nanostructure succeeds to use in the photocatalytic degradationand maximized for$Cd_{0.5}Zn_{0.5}Co_2O_4$ spinel oxide at 60 min (33%) and enhanced in basic condition (pH=13) to be 88%. The highest value of SSA found for $Cd_{0.5}Zn_{0.5}Co_2O_4$ spinel oxide ratio is the reason for its high photocatalysis activity.

Table1: the values of degradation efficiency (η) at 60 min, half time ($t_{1/2}$) and decomposition rate constant (K) for all the samples before and after pH- effect.

	Before pH effect			After pH effect		
x	***K*** **(min^{-1})**	$t_{1/2}$ **(min)**	***η*** **(%)**	***K*** **(min^{-1})**	$t_{1/2}$ **(min)**	***η*** **(%)**
0.00	$8.5*10^{-4}$	814	12	$2.2*10^{-2}$	31.5	87
0.25	$3.2*10^{-3}$	215	27	$2.3*10^{-2}$	30	86
0.50	$5.1*10^{-3}$	137	33	$1.9*10^{-2}$	36	88
0.75	$1.2*10^{-4}$	555	22	$2.1*10^{-4}$	33.5	82
1.00	$4.9*10^{-4}$	1395	6	$2.6*10^{-4}$	27	83

Credit authorship contribution statement:

Y. A. Taya; writing, formal analysis, validation, data curation, investigation and methodology, latifa Rashad; Experimental measurements, writing, software, formal analysis, M. I. Abd-Elrahman wrieting-review and editing A. Abu El-Fadl wrieting–review and editing, H. A. Mohamed supervision, wrieting-reviewand editing

All authors have read and agreed to the published version of the manuscript."

Data availability statement

The data used to support the findings of this study are available from the corresponding author upon request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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