

Research Article

Photocatalytic Degradation of Alizarin Red S by Using a Layered Zn/Al-NO₃ Double Hydroxides

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ABSTRACT

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This research presents the use of layered Zn-Al-NO₃ layered double hydroxides (LDH) which photocatalytically degraded Alizarin Red S (ARS) under a UV source. The prepared photocatalytic material was characterized by employing the use of X-Ray Diffraction (XRD) analysis, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX), Fourier Transform Infrared (FTIR) spectroscopy and Band gap Energy using Tauc plot. The analyzed XRD patterns of Zn-Al-NO₃ show characterized diffraction angles typical of LDH. Also, the XRD patterns were used to calculate the apparent crystallite size (32.5 nm). The bandgap energy of the LDH was determined to be 3.2 eV. The effect of the initial concentration of the ARS dye, catalyst amount or dose and pH were also determined. The Zn-Al-NO₃ efficiently degraded ARS at (69.91%), which could be attributed to its smaller crystallite size. The kinetic study (reaction rate and half-life) of the photodegradation appeared to be $R^2 = 0.9886$ and $t_{1/2} = 76.7$ min, the data fit the Langmuir Hinshelwood expression, which follows the pseudo-first-order kinetic model.

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INTRODUCTION

More than 40% of the population of Nigeria is depended upon some polluted surface water

for their domestic activities. If water cannot be used due to the presence of harmful substances, it is regarded as polluted water

Owa (2013). Degraded products of the dye and other unwanted compounds if found present in wastewater, could lead to skin ulceration, nausea, Hemorrhage and mucous membranes Solpan *et al.* (2003).

What could determine the treatment processes of the wastewater are: self-purification capacity of various streams, allowed levels of pollutants in water and economic interests of industries Rahim *et al.* (2015). A few of the various wastewater treatment processes are employed by various industrial sectors for the reasons of technology and economy Crini and Lichtfouse (2018). Out of the established processes, advanced oxidation process (AOP) has been included by EPA, as the best technology that can provide safer and sufficient pollution control for industrial remediation of pollutants Rashidi *et al.* (2014). According to Segneau (2013), several AOPs methods such as the photolysis, photocatalysis etc. have been known in the treatment of water and wastewater.

Enormous efforts have been devoted to modulating of the fine structure of active catalytic sites since this determines the activity and selectivity of catalysts Matsubu *et al.* (2017). Photocatalysts that can be used and reused as an adsorbent for environmental pollutants Zhao *et al.* (2020); Maimuna & Abdulfatah (2022), were still of practical interest. To date, several LDHs including Zn/Ce, Zn/Cr, Mg/Zn-Al, and Zn/Ga, Starukh (2017) have been used in the photodegradation of organic dyes Asouhidou *et al.* (2011).

Hence, the aim and objectives of the present research work are to prepare Zn/Al-NO₃ and to study the effect of various parameters of degradation such as the initial concentration, dose of photocatalyst and pH on photodegradation of Alizarin Red S dye under the ultraviolet source of irradiation.

METHODOLOGY

Synthesis of Layered Double Hydroxide

Zn-Al-NO₃ was prepared by the method of coprecipitation. An aqueous solution (100cm³) of NaOH (16.0g, 0.4mol) was added to an already prepared solution (150cm³) of Zn(NO₃)₂.6H₂O (44.6g, 0.15mol) and Al(NO₃)₃.9H₂O (18.8g, 0.05mol), with constant stirring until a final pH of 8.5 was reached. The as-prepared slurry was aged at 60°C for 24hrs, then finally centrifuged, and washed with water until the pH of the solution was decreased to near about 7. Then it was finally dried in an oven at 85°C for 24 hours.

Characterizations

X-ray diffraction patterns of LDH were taken by using a Phenomworld diffractometer with CuK α radiation over $2\theta = 5 - 70^\circ$ range at a rate of 2 mins. The Debye-Scherrer formula was applied to calculate the apparent crystallite size of the synthesized photocatalyst. The surface morphology of the synthesized material was examined by a scanning electron microscope (SEM, Phenomworld). Images were recorded at 15 kilovolts. The composition of the prepared LDH was determined by energy dispersive X-ray (EDX). The FTIR spectrum of Zn-Al-NO₃ was recorded using Agilent Microlab. The FTIR spectrum was recorded at a resolution of 4cm⁻¹ over the 4000 to 650 cm⁻¹ range. The Tauc Plot Method was used to determine the bandgap energy of the Zn-Al-NO₃.

Experiments

An initial experimental study was carried out to find out the most effective parameters towards photocatalytic degradation of alizarin red S and to optimize the dye using Zn/Al-NO₃. During each photocatalytic experiment, the aqueous suspension with 0.05 g of Zn/Al-NO₃ was continuously shaken for 10 mins in a dark to attain absorption-desorption equilibrium before the irradiation. In every experimental run, 100 cm³ of the aqueous solution of the dye alizarin red S (3, 6, 9 and

12 ppm) was taken in a photoreactor, under irradiation that was generated by mercury lamp (UV light source at a wavelength of 254 nm and power of 15 W) to activate the photocatalyst. At every interval of 10 minutes, 5 cm³ suspension of the sample was withdrawn, centrifuged for 15 minutes, filtered and analyzed by UV-Vis spectrophotometer (Jenway 6705 products). The degradation percentage was calculated from the initial and final concentrations of the UV-Vis data (Equation 1.0).

$$\%Degradation = \frac{C_0 - C_t}{C_0} \times 100 \quad (1.0)$$

Where

C₀= initial dyes concentration (mg/L) and C_t= concentration at irradiation time (t) in unit of mg/L.

RESULTS AND DISCUSSION

Photocatalyst characterization

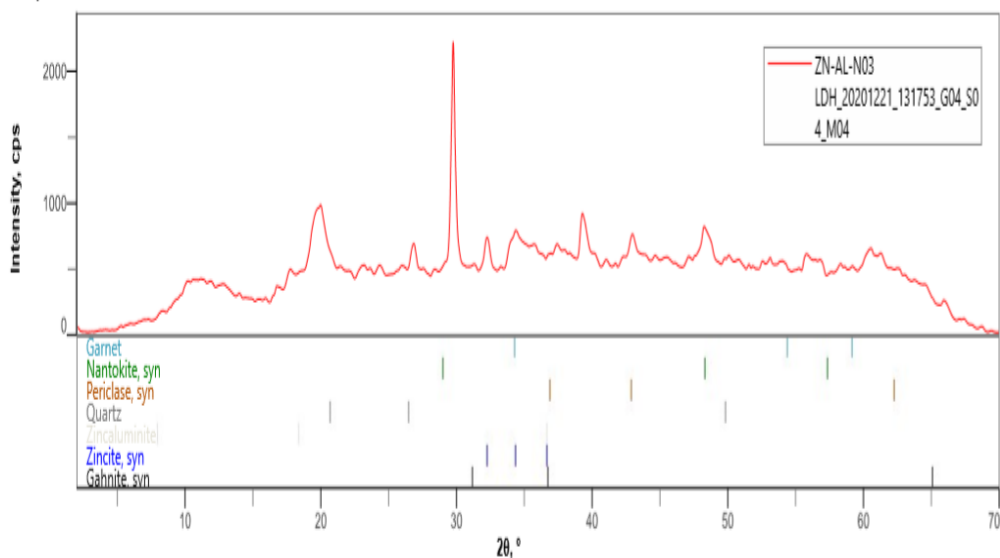


Figure 1: XRD pattern of Zn/Al-NO₃ photocatalyst

The XRD patterns of Zn/Al-NO₃ (Figure1) show characteristics of XRD diffraction angles of LDH 10°, 20°, 22°, 30°, 40°, 49° and 61° at 2θ. The peak at 61° is overlapped and the identified sharp peaks at 30° indicate interlamellar distance in LDH, this can be associated with a large quantity of Zn-O phase that is present in the LDH with a cation ratio of 3 as indicated by the presence of the peaks at angle 40°, 49° and 61°. According to

Abderrazek (2017), the crystallinity and the purity of the samples were dependent on the cationic ratio. The intensity of the peaks decreases with the increase in the cationic ratio.

The crystallite size is an important factor to be considered as it was calculated to be 32.5 nm sizes. The observed small crystallite size of the LDH may be attributed to a large degree of agglomeration during the synthesis.

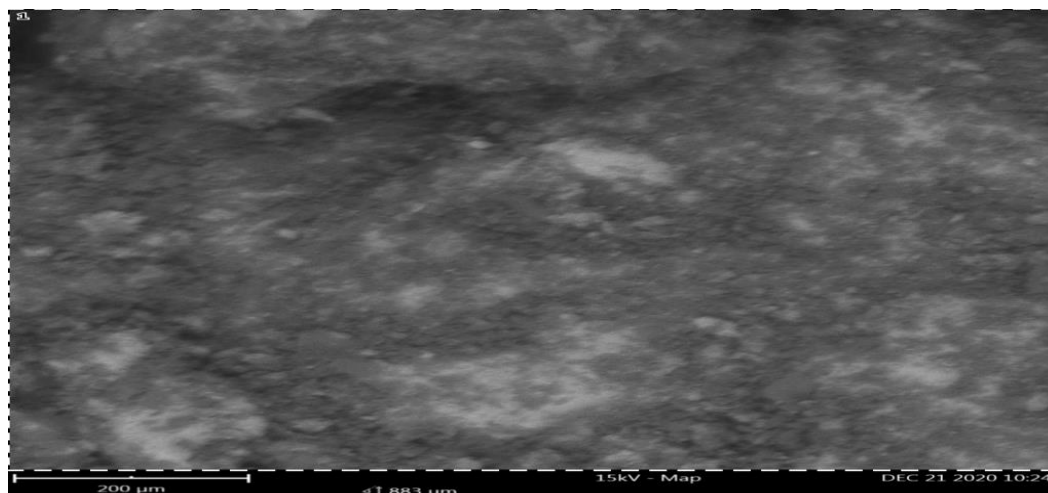


Figure 2: SEM image of Zn-Al-NO₃

The SEM image of the Zn-Al-NO₃ showed that it exhibited the characteristic of anionic clays (hexagonal plate-like habit) Starukh *et al.* (2016). From figure 2, it can be proven that

the Zn/Al-NO₃ have a lamellar structure which implied that the LDH can be obtained via coprecipitation Miranda *et al.* (2015); Todorova *et al.* (2014).

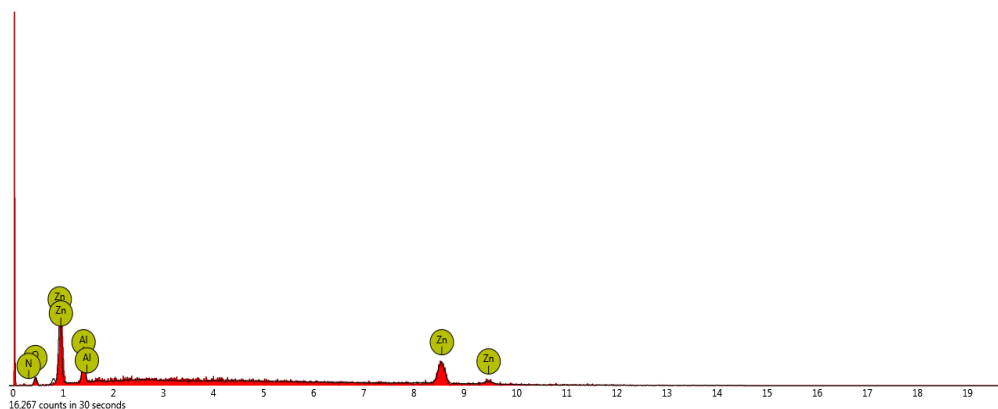


Figure 3: EDX spectrum of Zn/Al-NO₃ LDH photocatalyst

The EDX spectrum showed that Zn and Al (large quantity) were present in the synthesized LDH, while the N peak is present

in small quantity. The appearance of the peaks of oxygen has indicated the formation of metal oxides Rivera *et al.* (2006).

Table 1: Elemental composition of constituents in Zn-Al-NO₃

Element Number	Element Symbol	Element Name	Atomic Conc. %
30	Zn	Zinc	66.94
13	Fe	Aluminum	17.25
8	O	Oxygen	15.81
7	N	Nitrogen	0.49

Table 2: IR Characteristics of Zn-Al-NO₃

S/No.	Functional Group	Wavenumber (cm ⁻¹)
1.	-OH stretch	3365
2.	-OH bending	1640
3.	-N=O stretch	1339
4.	Zn-O	836

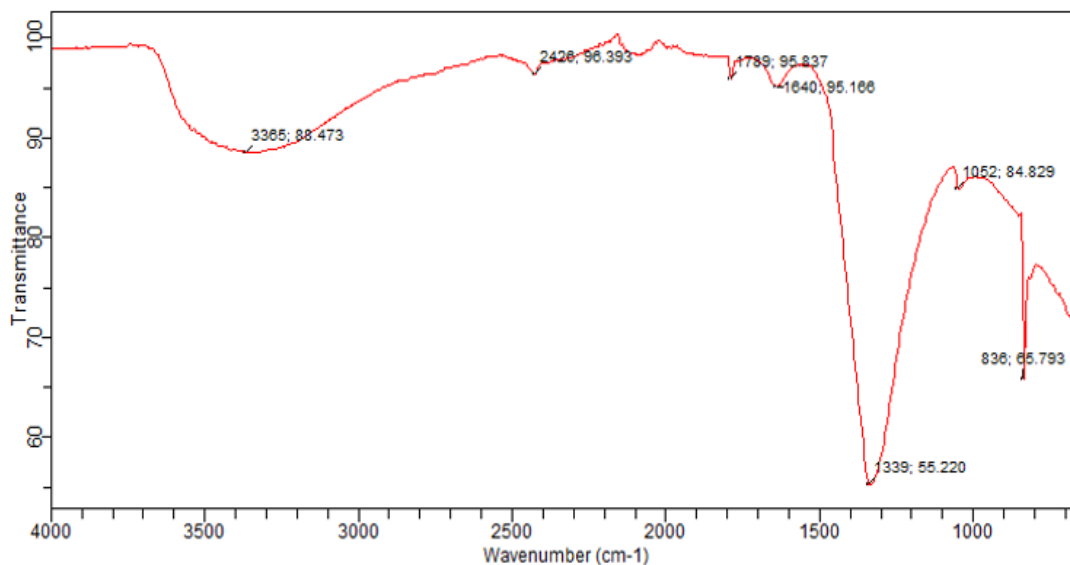
**Figure 4:** FTIR spectrum of Zn-Al-NO₃ photocatalyst

Table 2 shows the IR characteristics of the synthesized Zn-Al-NO₃. The FTIR spectrum (Figure 4) of Zn/Al-NO₃ shows a broad peak at 3365cm⁻¹ which was attributed to the -OH stretching of the hydroxyl groups and possibly water molecules. The identified weak band at

1640cm⁻¹ was assigned to bending vibration in water. The band at 1339cm⁻¹ wavenumber is corresponded to the symmetric stretching mode of interlayer in nitrate anions. The band at 836 cm⁻¹ assigned to ZnO translation Palapa *et al.* (2019).

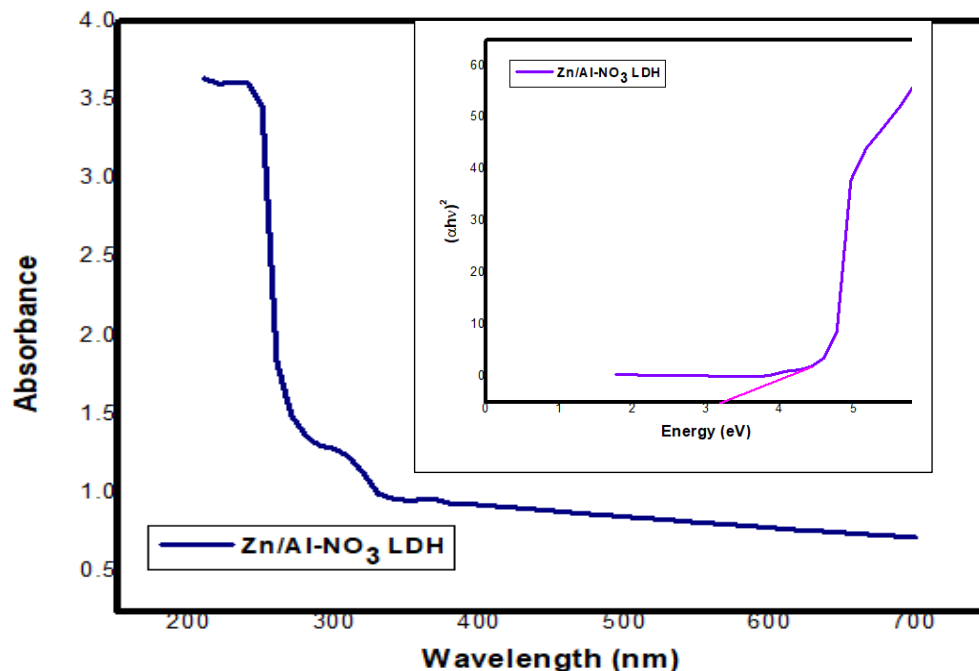


Figure 5: UV–Vis curve for Zn-Al-NO₃ and Tauc Plot

As displayed in (Figure 5) the band gap energy value of Zn/Al-NO₃ was determined to be 3.2 eV. This value was close to the value obtained by Abderrazek (2015), in Zn/Al

photocatalytic studies. The result of this analysis was also consistent with the operational parameters.

Operational parameters

Effect of dye Initial concentration

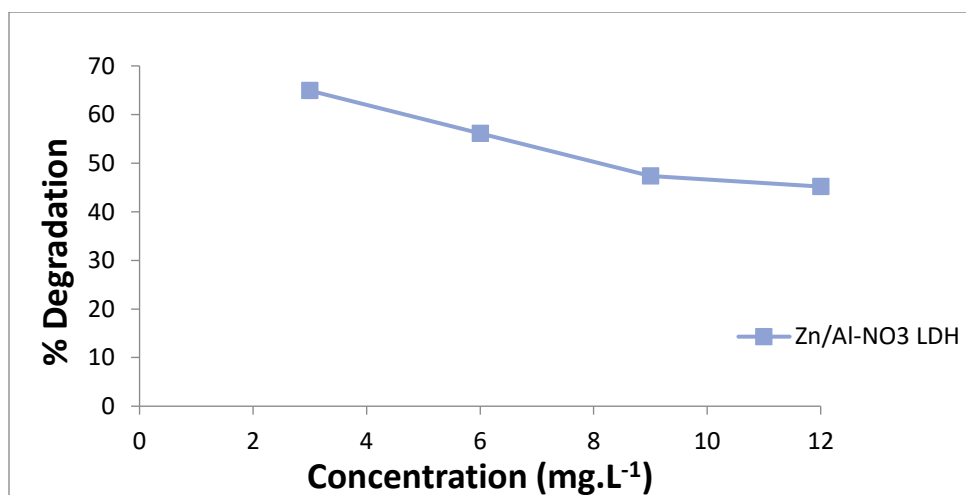


Figure 6: Effect of Initial Concentration of Alizarin Red S Dye.

The effect of concentration on photocatalytic degradation of ARS dye under a constant irradiation time and catalyst dose was

investigated at various dye concentrations (3, 6, 9 and 12 mg.L⁻¹) at constant time of 40 min and catalyst dose (0.05 g Zn/Al-NO₃). The

photodegradation of the dye was found to have decreased as the initial concentration of ARS dye increased. From Fig. 6, the result has revealed that at $3\text{mg}\cdot\text{L}^{-1}$, Zn-Al-NO₃ was found to degrade 69.91 % of the ARS dye. By increasing the concentration to $12\text{mg}\cdot\text{L}^{-1}$, the photocatalyst has tended to decrease the degradation rate up to 45.17 %.

This decreased efficiency of the photocatalyst might be because as the initial dye concentration increased, there would be more and more dye molecules that will be adsorbed on the surface of the photocatalyst and

therefore, a significant amount of UV-light will be absorbed by molecules of dye rather than the photocatalyst itself, and consequently, light penetration to the Zn/Al-NO₃ surface decreases. Due to this process, the generation of hydroxyl radicals tends to decrease as the active sites were more occupied by dyes. The finding here is consistent with the study of photocatalytic degradation of Alizarin Red S reported by Saeed (2018), in which the best degradation efficiency was obtained when the initial dye concentration is low.

Influence of Zn/Al-NO₃ dose

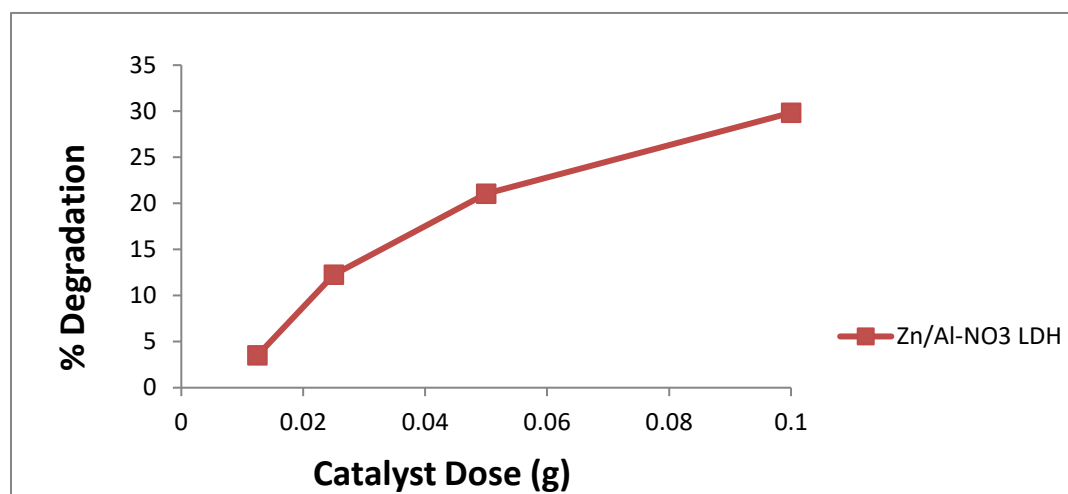


Figure 7: Influence of Zn/Al-NO₃ on Photodegradation of Dye

The influence of the Zn/Al-NO₃ dose on the degradation of ARS dye was explored under UV light at different dosages of the photocatalyst and at a constant concentration of $3\text{mg}\cdot\text{L}^{-1}$. Fig. 7 shows the degradation efficiency at different dose. The figure reveals that the efficiency increased greatly by

increasing the amount of the photocatalyst from 0.01 g to 0.1 g. The maximum degradation of 29.82 % was observed with 0.1g dose of Zn-Al-NO₃. This result is in line with the result from Amalraj & Pius (2014) in their photodegradation studies of dyes.

Influence of pH

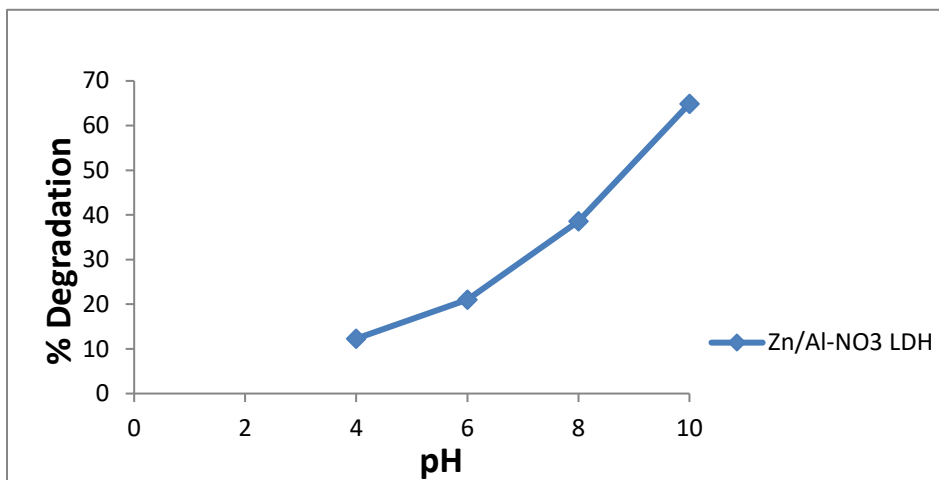


Figure 8: Influence of Solution pH on the Degradation of Alizarin Red S.

In order to study the influence of pH on the photodegradation of ARS using Zn/Al-NO₃, pH values ranging from 4-10 were maintained at constant ARS concentration (3 ppm) and catalyst dosage (0.05 g). It is observed from Fig. 8 that at acidic pH the degradation efficiency of Zn/Al-NO₃ is low because of partial dissolution of photocatalyst Senthilraja

et al. (2015) as it showed 12.3 % efficiency. Bahu (2014) reported 76.53 % efficiency of Bi₂O₃ for photodegradation of ARS dye under UV light illumination in the year 2014, whereas in the current study the efficiency of Zn/Al-NO₃ at basic pH was found to be 64.9 %.

Kinetics study

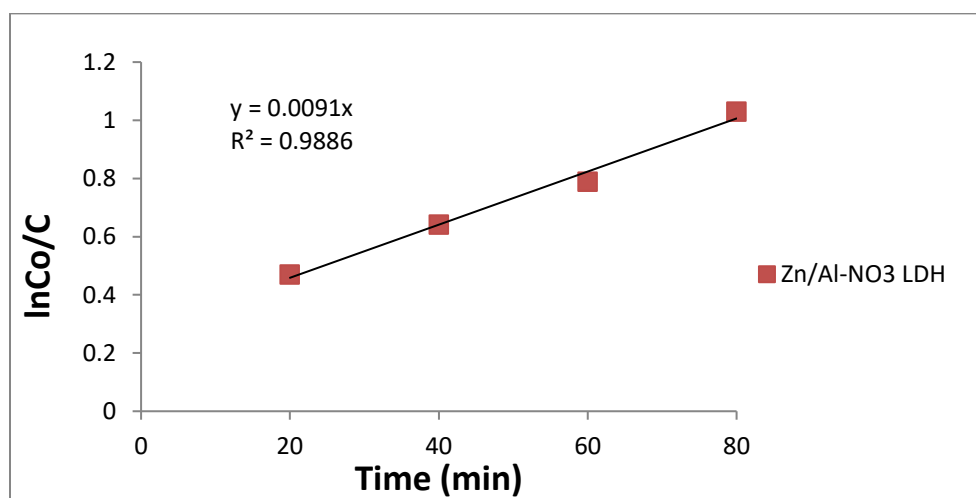


Figure 9: Kinetics of Degradation of Alizarin Red S using Zn/Al-NO₃.

CONCLUSION

In this study, it can be concluded that Zn-Al-NO₃ was successfully prepared via a co-

precipitation method. Experimental results showed the effectiveness of Zn-Al-NO₃ on the photodegradation of ARS. The photocatalytic degradation of ARS has only taken place with

the presence of the LDH dose, without the photocatalyst it might take a very long time to photodegrade, as for initial concentration of ARS, it can be deduced that the percentage degradation is higher when the concentration of the solution is lower. The maximum degradation efficiency of ARS was obtained in basic pH medium. Kinetic study showed that the photocatalytic process fits with pseudo first-order of the Langmuir Hinshelwood model which is commonly used to describe the kinetics of photocatalytic reaction of organic compound in aqueous solution and the low bandgap energy influenced good

photocatalytic activity of Zn/Al-NO₃. Therefore, the observations that are made in above imply the great potential for used of this LDH in wastewater treatment application.

Declaration of Interest

There is no conflict of interest to declare.

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