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Zn/Fe-NO_3 LAYERED DOUBLE HYDROXIDES: SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY ON PHENOL RED DEGRADATION

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ABSTRACT

Zn/Fe-NO_3 layered double hydroxides (LDH) photocatalyst was successfully synthesized via co-precipitation method and used to optimize the photocatalytic degradation of Phenol Red (PNR). The synthesized photocatalyst was characterized using X-Ray Diffractometer (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX) spectrophotometer, Fourier Transform Infrared (FT-IR) spectrophotometer and Bandgap Energy. The XRD patterns of Zn/Fe-NO_3 show characteristic diffraction angles of LDH which indicate features of well synthesized LDH. The XRD patterns were also used to calculate the apparent crystallite size of the LDH using Debye-Scherrer's formula and it was calculated to be 31.0 nm. Bandgap energy of the LDH was determined by extrapolating the linear region to the x-axis of the Tauc plot to be 2.5ev. Zn/Fe-NO_3 was used to study the effect of various operational parameters, initial dye concentration, catalyst dose and pH. The Zn/Fe-NO_3 LDH photocatalyst exhibited high photocatalytic activity, when an excellent degradation of PNR was achieved with 96.75%. The optimum degradation was obtained when 0.1g dose Zn/Fe-NO_3 LDH was used to degrade 3ppm PNR. The kinetic study of the photodegradation fits Langmuir Hinshelwood expression which follows pseudo-first order model with the correlation coefficient, R^2=0.9982 and half-life ($t_{1/2}$) = 145.5 min respectively.

Keywords: Degradation, Layered double hydroxides, phenol red, photocatalysis.

INTRODUCTION

The widespread occurrence of phenols in waste water and associated environmental hazards has heightened concern over public health. Phenols and their derivatives are well known for their bio-recalcitrant and acute toxicity [1]. Moreover, toxicity data reveal that phenol red inhibits the growth of renal epithelial cells. Direct or indirect contact with the dye leads to irritation to the eyes, respiratory system, and skin. Thus keeping the toxic effects of the dye in view attempts have been made to develop an efficient and low cost effective technique for the

degradation of dye from wastewater [2]. At the turn of the last century, the most common wastewater treatments were based upon a combination of mechanical, biological, physical and chemical processes such as filtration, flocculation, chemical or biological oxidation of organic pollutants [3]. However, each treatment has its own constraints not only in terms of cost, but also in terms of feasibility, efficiency, practicability, reliability, environmental impact, sludge production, operation difficulty, pre-treatment requirements and the formation of potentially toxic byproducts. In view to suppress the worsening of clean water shortage, development of advanced with low-cost and high efficiency water treatment technologies to treat the wastewater is desirable [4]. Advanced oxidation processes such as heterogeneous photocatalysis are applied for wastewater treatment. Radicals are generated during the process, as powerful oxidizing agent and are expected to sufficiently destruct wastewater pollutants. Consequently, transform them into less and even non-toxic products, thereby providing an ultimate solution for wastewater treatment [5]. In this present study, a relatively new photocatalyst Zn/Fe-NO_3 with band gap 2.5 eV, have been utilized efficiently in degradation of phenol red. Literature survey revealed that, no attempt has been made for photocatalytic degradation of this dye using Zn/Fe-NO_3 under UV-visible irradiation.

EXPERIMENTAL

Synthesis of Zn/Fe-NO_3 LDH

Zn/Fe-NO_3 was synthesized by co-precipitation method. An aqueous solution (100cm^3) containing NaOH (16.0 g) was added to a solution (150 cm^3) containing $Zn(NO_3)_2.6H_2O$ (44.6g) and $Fe(NO_3)_3.9H_2O$ (20.2 g) (initial Zn/Fe = 3.0) with continuous stirring until the final pH of 8.5 is reached. The resulting slurry is aged at 60 ºC over night and then centrifuged and washed with distilled water until the pH decreased to 7, and finally it as dried in an oven at 85 ºC for 24 hours. The sample was donated as Zn/Fe-NO_3 layered double hydroxides.

Characterization of Photocatalyst

X-ray diffraction patterns of the LDH were recorded using PhenomWorld diffractometer having CuKα radiation (λ= 1.56Å) in the 2θ range of 5 - 70^0 with scanning rate of 2 minutes. Calculation of apparent crystallite size of the LDH has been performed by Debye-Scherrer formula: $\beta(2\theta) = 0.94\lambda/(D\cos\theta°)$, and employing the FWHM procedure. The morphology of the synthesized LDH was examined by a scanning electron microscope (SEM, PHENOMWORLD). Image was recorded at 15kv. The elemental composition of the

synthesized LDH was determined by energy dispersive x-ray (EDX). The FTIR spectrum of Zn/Fe-NO_3 LDHwas recorded using Agilent Microlab. The spectra were recorded at resolution of 4cm^{-1} in the range of 4000-695cm^{-1}. And bandgap enerygy of the photocatalyst (Zn/Fe-NO_3 LDH) was also determined using Tauc Plot Method.

Photocatalytic experiments

The photocatalytic experiment was performed when an aqueous suspension with a definite amount of Zn/Fe-NO_3 LDH photocatalyst was stirred continuously for 10 min in dark to attain absorption-desorption equilibrium prior to irradiation. In each experimental run, 100 cm^3 aqueous solution of phenol red (3, 6, 9 and 12 ppm) containing a specified amount of the photocatalyst (0.05 g/L) were taken into a photoreactor (under irradiation generated by mercury lamp (UV light source at 254 nm with definite power of 15 W) for activation of the photocatalyst. At given time intervals, 5 cm^3 sample of the suspension were withdrawn, centrifuged for 15 min and filtered to remove the solid phase using 0.7μm filter paper and analyzed using UV-Vis spectrophotometer with cuvette 1cm path length (Jenway 6705 products) and the blank reaction was also carried out by the same procedure without adding any LDHs. The percentage degradation of the initial dye concentration was calculated using Equation 1.0.

$$\%Degradation = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Where C_o= initial dyes concentration, C_t = concentration at irradiation time (t).

RESULTS AND DISCUSSION

X-ray diffraction of LDH

The XRD patterns of Zn/Fe-NO_3 LDH. Figure 1, shows characterized diffraction angles of the LDH at 10.2º, 29º, 33, 39º and 48º angles. The sharp peaks at 29º indicate interlamellar distance of LDH, which is associated with ZnO phase formed on the surface of the brucite-like sheet. This is indicating large quantity of ZnO phase is present in the LDH. This result is in good agreement with the EDX analysis result. The crystallite size was calculated to be 31 nm. The small crystallite size detected from XRD pattern and Scherrer's formula facilitated the rapid transfer of photoelectrons from bulk to the surface. This effectively inhibit the recombination between photoelectrons and holes, leading to the improvement of photocatalyst activity [6].

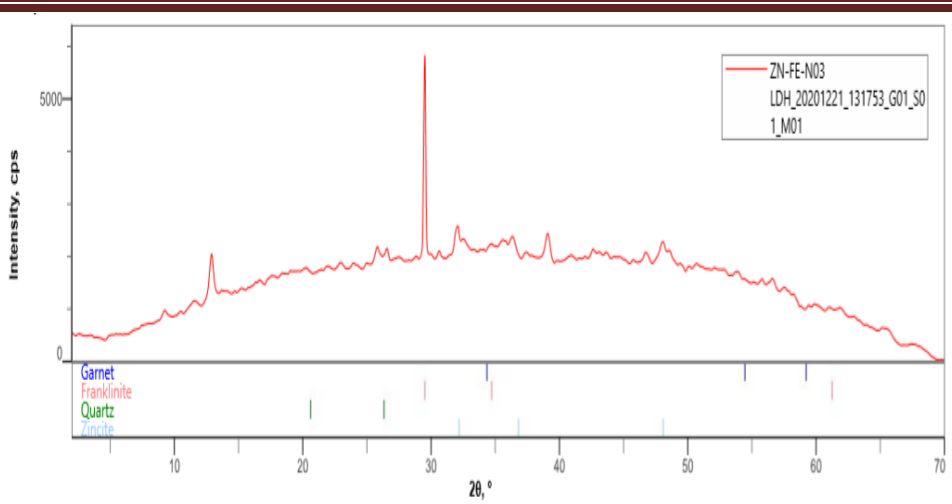

Figure 1: XRD pattern of Zn/Fe-NO_3 LDH

Scanning Electron microscopy of LDH

The SEM micrograph of the prepared Zn/Fe-NO_3 LDH photocatalyst (Figure 2) shows that the material is formed by an agglomeration of nearly spherical particles. The agglomerated pattern is evidence in the formation of LDHs and the morphology of the LDH is in line with the synthesized LDHs reported by Starukh *et al* [7].

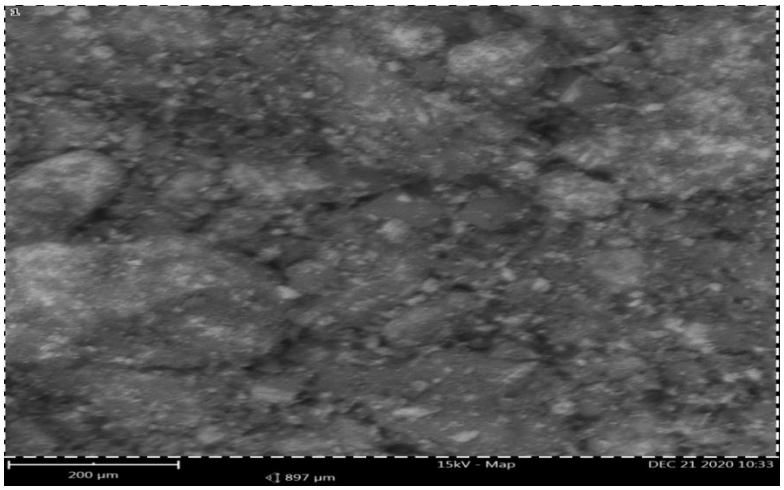

Figure 2: SEM Micrograph of Zn/Fe-NO_3 LDH

Energy dispersive x-ray

The EDX spectra show the presence of Zn and Fe in large quantity and N peak is present in small quantity. The presence of oxygen peak indicates the formation of metal oxide and functionalization of Zn/Fe-NO_3LDH during the treatment, which introduced nitrogen oxide functional group.

Table 1: Weight and Atomic Percentage of the Constituents of Zn/Fe-NO_3, Zn/Al-NO_3 LDHs

Element Number	Element Symbol	Element Name	Atomic Conc. %
30	Zn	Zinc	66.94
26	Fe	Iron	23.25
8	O	Oxygen	9.35
7	N	Nitrogen	0.47

Infrared Characterization of LDH

The FTIR spectra of Zn/Fe-NO_3 LDH shows accordingly the peaks at 3569-3476cm^{-1} are attributed to the stretching of the OH bond of the hydroxyl groups and H_2O molecules. The weak band at 1637cm^{-1}can be assigned to the H_2O bending vibration of the interlayer water. The band at 1346cm^{-1} corresponds to the symmetric stretching mode of the interlayer nitrate anions. As the amount of nitrate provided by the precursors used for the synthesis of LDHs is important, we expect that nitrate peaks to appear. The band 836cm^{-1}can be assigned to Zn-O band, while the peak at 695-676cm^{-1} can be assigned to Fe–O band. The assignments of the other bands are somewhat controversial. Thus, the above mentioned observation clearly indicates the successful formation of Zn/Fe-NO_3 LDH [8].

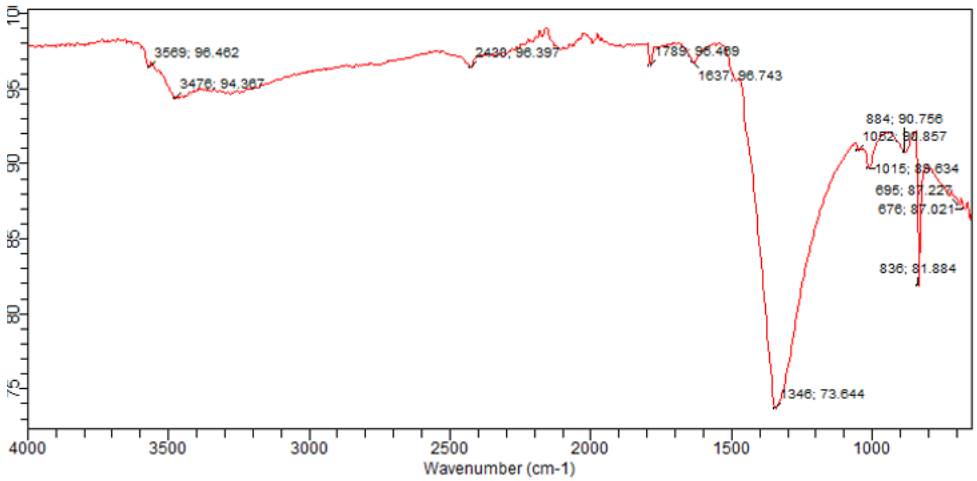

Figure 3: FTIR spectra of Zn/Fe-NO_3 LDH photocatalyst

Table 2: Fourier Transform Infrared Spectroscopic Data for Zn/Fe-NO_3 LDH.

Functional Groups	Zn/Fe-NO_3 LDH Wavenumber (cm^{-1})
O-H	3569-3476
O-H	1637
N-O	1346
Zn-O	836
Fe-O	695-676

Bandgap energy of LDH

As showed in (Figure 4), the band gap energy value for the Zn/Fe-NO_3 LDH was 2.5ev. This value was close to those obtained for Zn/Fe-NO_3 LDH photocatalytic studies by Xia *et al* [9]. The bandgap energy of Zn/Fe-NO_3 LDH appeared to be narrow this implies that the photoadsorption and higher photocatalytic activity of Zn/Fe-NO_3 LDH was strong.

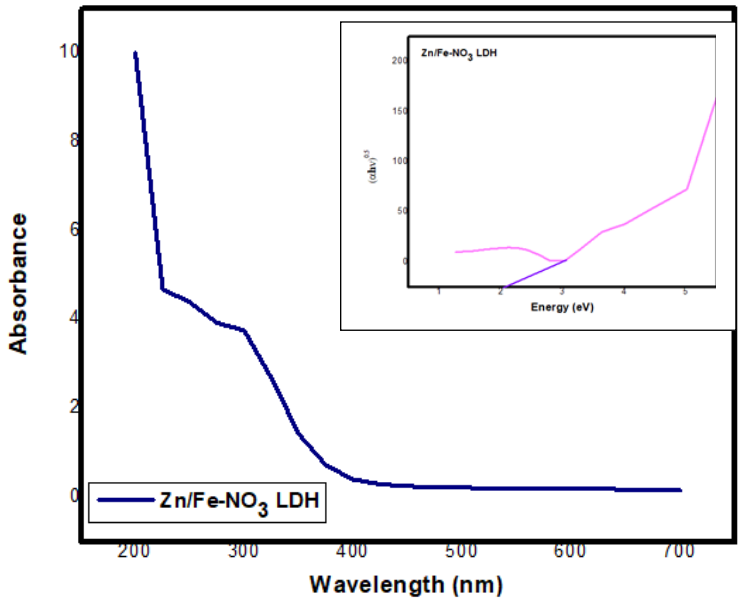

Figure 4: The UV–vis curves for Zn/Fe-NO_3 LDH and Tauc Plot.

Effect of initial dye concentration

It was observed that photodegradation of dye decreased as initial dye concentration of phenol red dye increased. From Figure 5, the results revealed that at 3 ppm Zn/Fe-NO_3 LDH degraded about 96.75% of the dye. Increasing dye to 12 ppm decreased degradation rate to 62.60%. This decreased efficiency of the LDH might be due to the fact that as the initial dye concentration increased more and more dye molecules will be adsorbed on photocatalyst surface and significant amount of UV-light will be absorbed by the dye molecules rather than the

photocatalyst and, consequently, light penetration to Zn/Fe-NO_3 LDH surface decreases. Due to this phenomenon, generation of hydroxyl radicals decreases as the active sites were occupied by dye. This finding is in good agreement with the findings reported by Xia *et al* [10].

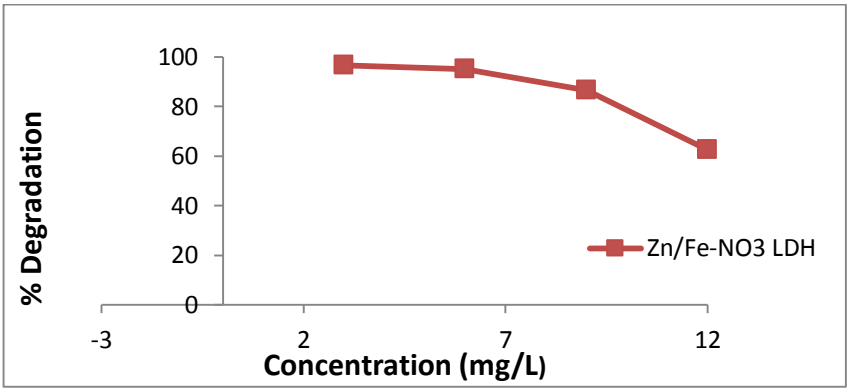

Figure 5: Effect of Initial Phenol Red Dye Concentration

Effect of catalyst dosage

The effect of photocatalyst dose on the degradation efficiency of phenol red was investigated under UV light employing different dosages of Zn/Fe-NO_3 LDH at a fixed dye concentration of 3 ppm. The degradation efficiency of LDH dose on phenol red is illustrated in Figure 6, which reveals that the efficiency increased greatly by increasing catalyst dosage from 0.025g to 0.1g and thereafter the rate of degradation remains almost constant. Maximum degradation was observed with 0.1 g dose of Zn/Fe-NO_3 LDH as 30.08%. With high dose of photocatalyst turbidity of the suspension increases, there will be a decrease in the penetration of UV light and hence photoactivated volume of suspension decreases [11-12].

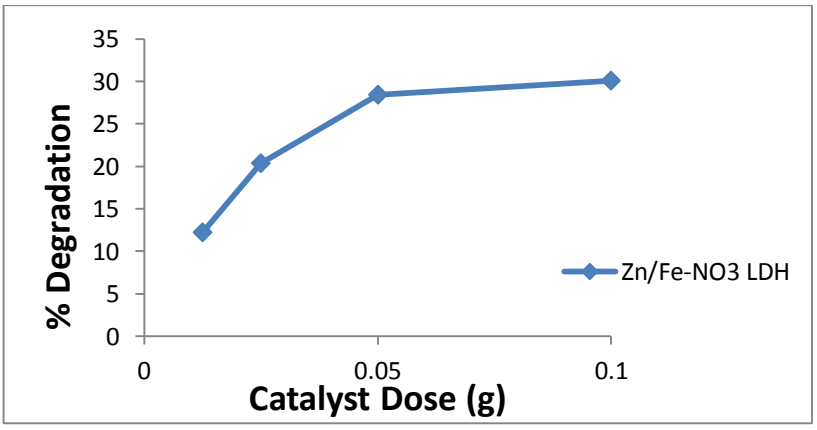

Figure 6: Effect of Amount of Zn/Fe-NO_3LDH on Photodegradation of Phenol Red Dye

Effect of pH

pH is the most important parameter in the photocatalytic reactions taking place on particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst. The higher uptake of the phenol red percentage degradation was observed to be in the acidic medium and was found to be 85.3% in presence of Zn/Fe-NO_3 LDH. This result is in line with result obtained by Wahab *et al* [13] where phenol red degradation was favorable at mild acidic solution (pH = 4.5). Similar results were reported by Asiri *et al* [14] for the maximum photodegradation of phenol red on TiO_2 under solar irradiation at value of acidic pH. The improved efficiency for the degradation of phenol may be due to the fact that under acidic or alkaline condition the surface of photocatalyst can be protonated or deprotonated respectively [15]. The consideration of the results above mentioned, reveals the photocatalytic efficiency of Zn/Fe-NO_3 LDH under UV illumination.

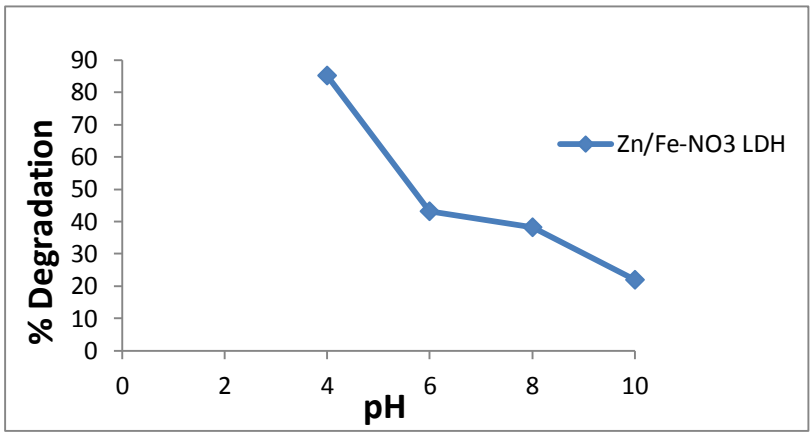

Figure 7: Effect of pH on the Photodegradation of Phenol Red Dye

Kinetic study

Accordingly, the rate constant and the half-life were calculated to be k = 0.0048 $mgL^{-1}min^{-1}$and half-life= 145.5 min. The regression correlation coefficient R was 0.9982, which suggest the photodegradation of phenol red dye by Zn/Fe-NO_3 fits the Langmuir-Hinshelwood kinetic expression well. The half time and the observed rate constant for the degradation of studied dye were inversely proportional with the rising in the initial dye concentrations ranged from 3 ppm to 12 ppm. These data provide the better agreement with the results that is reported by Kzar *et al* [16], for degradation of Metanil Yellow dye so they found a tendency toward independent values with the higher initial concentrations. This behavior is interpreted to depress the reached light in solution, hence only fewer light photons

will reach to catalyst surface, which led to limit the hydroxyl and superoxide radicals formed [17].

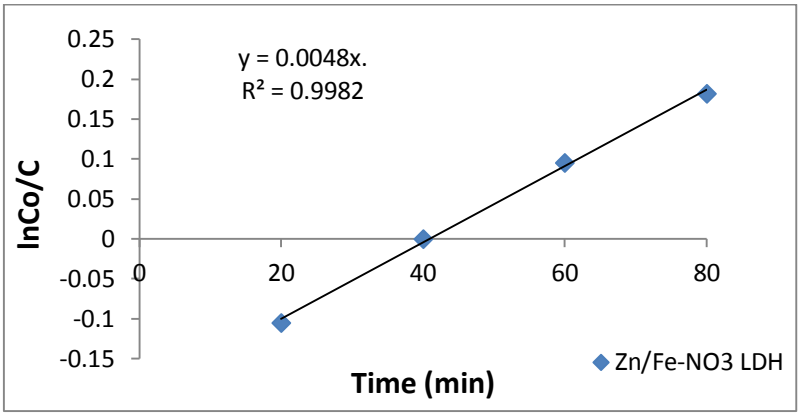

Figure 8: Langmuir-Hinshelwood Plot for Degradation of Phenol Red using Zn/Fe-NO_3 LDH

CONCLUSION

Zn/Fe-NO_3 was successfully prepared via a co-precipitation method and characterized using XRD, SEM, EDX, FT-IR analysis and Bandgap Energy determination. The presence of the anions in the hydrotalcite structure was confirmed by infrared spectroscopy. The XRD analyses showed the crystallite size and bandgap energy improved the photocatalytic activity of the LDH. The degradation of the dye was found to be sensitive to the operational parameters. The ultraviolet (UV) light irradiation of the dye with Zn/Fe-NO_3 as a photocatalyst has yielded percentage degradation of greater than 70% for a catalyst dosage of 0.1g/L and initial concentration of the dye solution of 3ppm. This can be an efficient and cost effective method of treating wastewater. The maximum degradation of phenol red was obtained in an acidic pH solution. Based on the results, Kinetic study showed that the photocatalytic process fits with pseudo first-order of the Langmuir Hinshelwood model based on correlation coefficient. Therefore, it is concluded the LDH can be used to degrade organic contaminants in aqueous medium.

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