



## Research Article

# Synthesis, Characterization and Photocatalytic Activity of Eco-friendly ZnCr/C-LDH Nanocatalyst

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### ARTICLE INFO:

#### Keyword:

Layered double Hydroxide, UV-irradiation, Catalyst recovery, Congo red

### ABSTRACT

ZnCr/C layered double hydroxide (LDH) was synthesized using the co-precipitation method. The LDH photo-Catalyst was characterized using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy dispersive Spectroscopy (EDS), Fourier transformed infrared (FTIR) and Thermo gravimetric analysis (TGA). The  $2\theta$  values at 13.5, 24.5 and 32.5 in XRD confirmed the formation of the Layered double hydroxide structure. The lower band gap energy at 1.84eV suggests that the catalyst works well in the UV-visible region. The photocatalytic activity of the LDH under UV-Irradiation in aqueous Congo red (CR) was studied under optimal operational parametric conditions (Concentration, catalytic dosage and pH). The kinetics of the photocatalytic activity was investigated using the Langmuir-Hinshelwood model. The LDH Shows excellent recyclability, durability and stability even after the fourth cycle.

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## INTRODUCTION

Removing atmospheric and aquatic pollutants is one of the major environmental problems (Sivalingham *et al.*, 2003), many researchers have investigated a means of removing dyes but photo-catalysis provides a promising solution for effective dye removal (Hadnadjev *et al.*, 2010). The photo-catalytic reaction involves the use of light to excite electrons from the valence band to the conduction band and a combination of the photo-generated holes with H<sub>2</sub>O and OH<sup>-</sup> to generate OH radical (Fujishima *et al.*, 2008). The generated radicals are very active specie which oxidizes and completely mineralise the dyes into water and carbon dioxide. Photo-catalysts are very effective, non-toxic, have high oxidative power and are stable to light (Crisan *et al.* 2008). Recently layered double hydroxide LDH is widely used as either photo-catalyst or photo-catalyst support because it is very effective and eco-friendly (Seftel *et al.*, 2008). LDH has a wide range of application fields that include Nano-composite (Garzali and Muhammad, 2019) adsorption (Bruna *et al.*, 2009), electrochemistry (Guida *et al.*, 1997), catalysis (Mousty and Leroux, 2013) and medicine (Choy *et al.*, 2006).

LDH compounds have various transition elements such as Zn (Zhao *et al.*, 2012), Ti, Ga

(Lee *et al.*, 2011), Y (Ahmed *et al.*, 2011), In (Teramura *et al.*, 2012), homogeneously dispersed into the interlayer LDH were investigated, showing specific surface areas, high thermal stability and semiconducting properties.

In particular, since ZnCr-LDH compound was reported as an efficient photocatalyst for visible light photocatalytic activities (Mohapatra and Parida, 2012) a peculiar attention has been paid to Cr (III) based LDH. In an excellent approach, Gunjekar *et al.*, 2011). (Gomes-Silva *et al.*, 2009) used a self-assembly process to associate positively charged ZnCr nanosheets and negatively charged layered titanium oxide to improve the ZnCr – photocatalytic efficiency. LDH has received much attention in the scientific field due to its varied catalytic application. Various Zn-based LDHs have been used for dye degradation in the literature, copper phthalocyanine-immobilized Zn/Al-LDH was used for the degradation of methylene blue (MB) dye under solar light irradiation (Parida *et al.*, 2007) and Zn-Cr-LDH under visible light irradiation has been used for the degradation of organic pollutants (Mohapatra and Parida, 2012).

The motivation for this work is to synthesize, characterize and investigate the photocatalytic activity of ZnCr/C on the removal of Congo Red (CR) using ZnCr/C.

## MATERIALS AND METHODS

### Synthesis of Zn-Al/C-LDH

The LDH nanostructure was wrapped in activated carbon through a co-precipitation method, Salts of CrCl<sub>3</sub> and ZnCl<sub>2</sub> were mixed in a 1:3 molar ratio. Prior to mixing, 250cm<sup>3</sup> of 0.1M CrCl<sub>3</sub> was mixed with 250cm<sup>3</sup> of 0.3M ZnCl<sub>2</sub> in 1000cm<sup>3</sup> beaker. 10 wt% of activated carbon was added to the solution mixture and

was dispersed by a magnetic stirrer. The pH was adjusted to 9 by the drop-wise addition of 0.1M NaOH solution. The mixture was aged overnight. The resulting precipitate was filtered and washed with a C<sub>2</sub>H<sub>5</sub>OH: H<sub>2</sub>O mixture (8:2). The product was then dried overnight in an oven at 53°C (Garzali and Muhammad, 2019).

### Characterization

The XRD data was analyzed using Full Proof Suite 3.0. Both SEM and EDS were carried out using the same machine (JEOL JEM-2010). FT-IR was carried out using FTIR-Cary 630 TGA analysis was carried out using a TGA machine (Agilent Technologies).

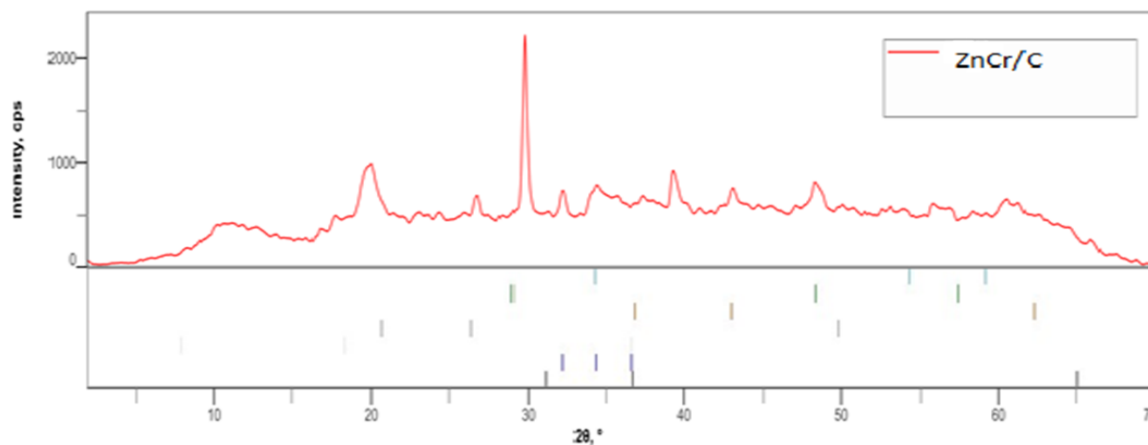
from Agilent technologies was used and the spectra were recorded in the wavelength interval 4000 to 750  $\text{cm}^{-1}$ . The band gap energy determination was achieved using UV-Visible spectroscopy Perkin Elmer Lambda 35.

### Photocatalytic Experiment

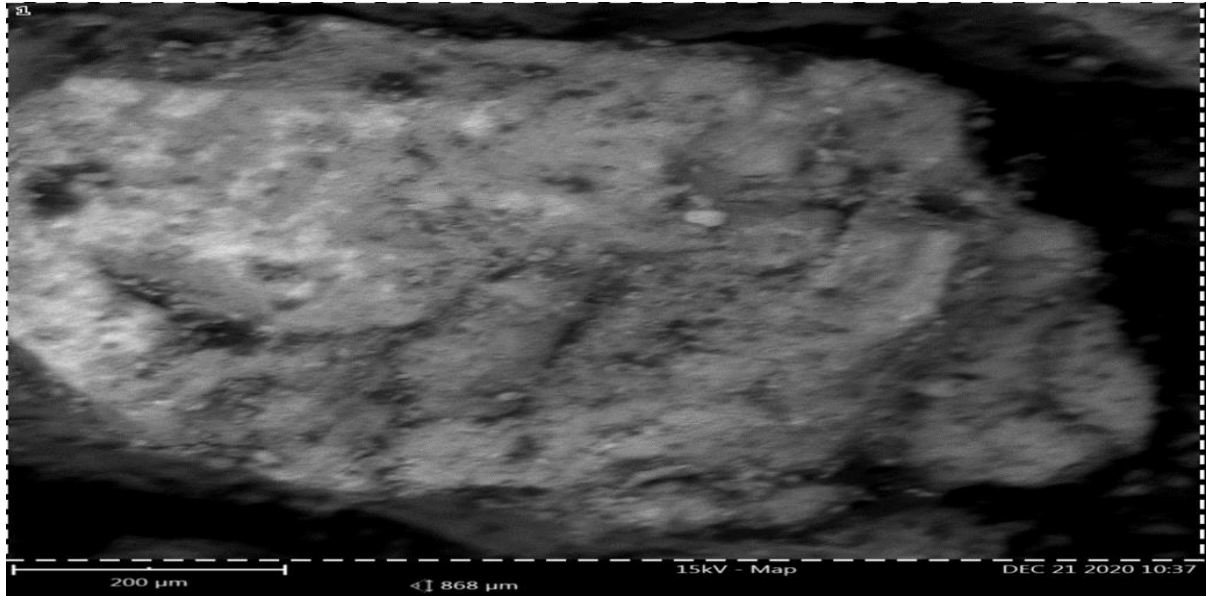
In this experiment, 80mg of Zn-Cr/C has dispersed in 3ppm of Congo red (CR) dye solution. The above suspension was magnetically stirred for 35mins in the dark to obtain adsorption-desorption equilibrium to remove any error due to the adsorption technique. The mixture was then irradiated using a 50Hz UV lamp at 365nm. A 10 $\text{cm}^3$  aliquot was taken at 20mins intervals, centrifuged at 250rpm and filtered before absorbance measurement to eliminate error due to scattering (Mohapatra and Parida, 2012). The catalytic activity of Zn-Cr/C was evaluated against CR under Ultra-violet light.

## RESULTS

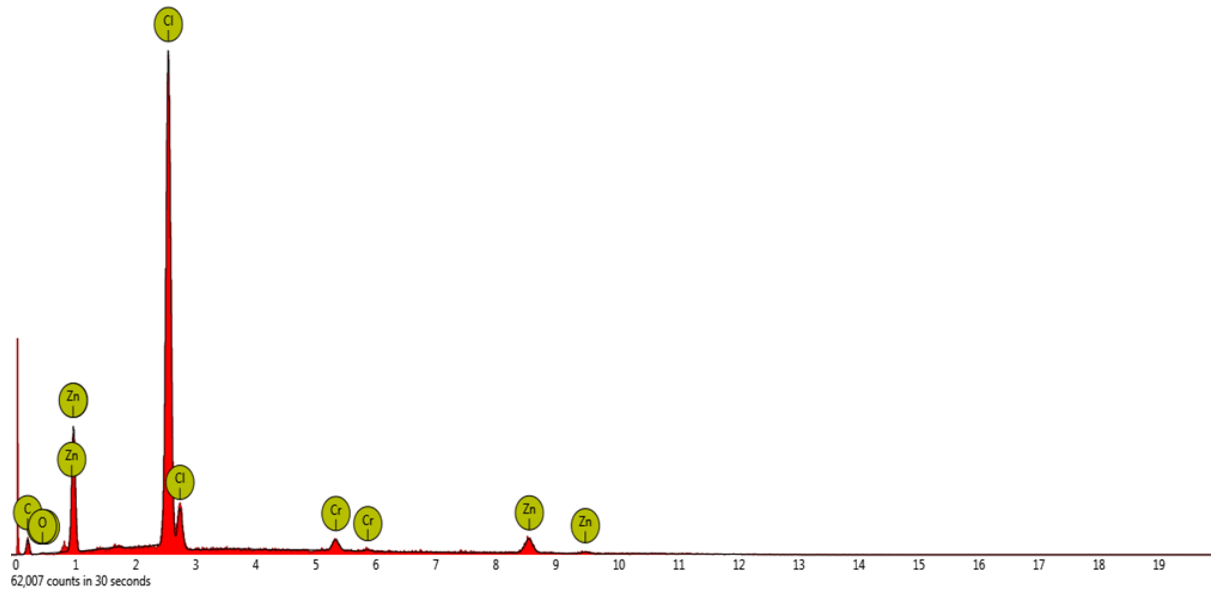
The results include experimental results and characterization.



**Figure 1:** XRD pattern of ZnCr/C



**Figure 2:** SEM image of ZnCr/C



**Figure 3:** EDS Spectrum of ZnCr/C

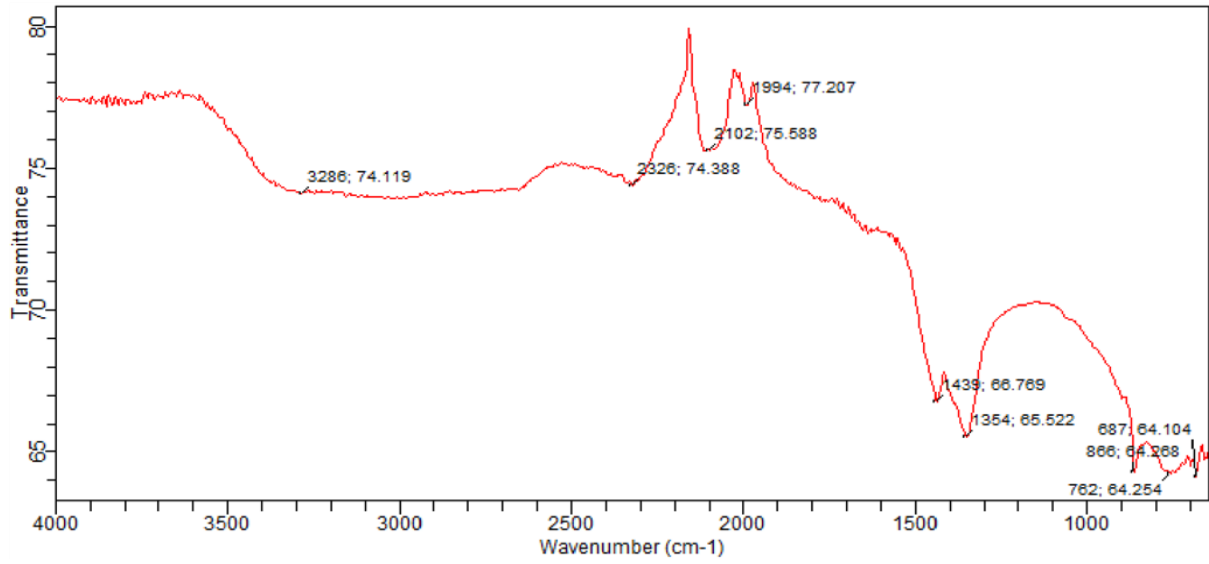


Figure 4: FTIR Spectrum ZnCr/C

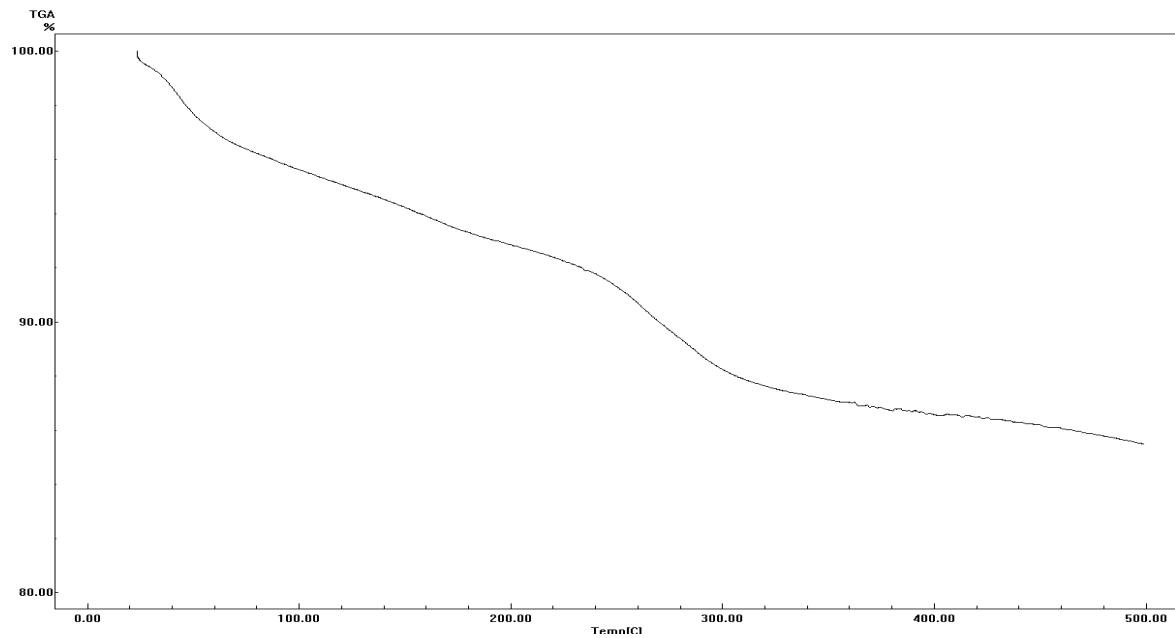
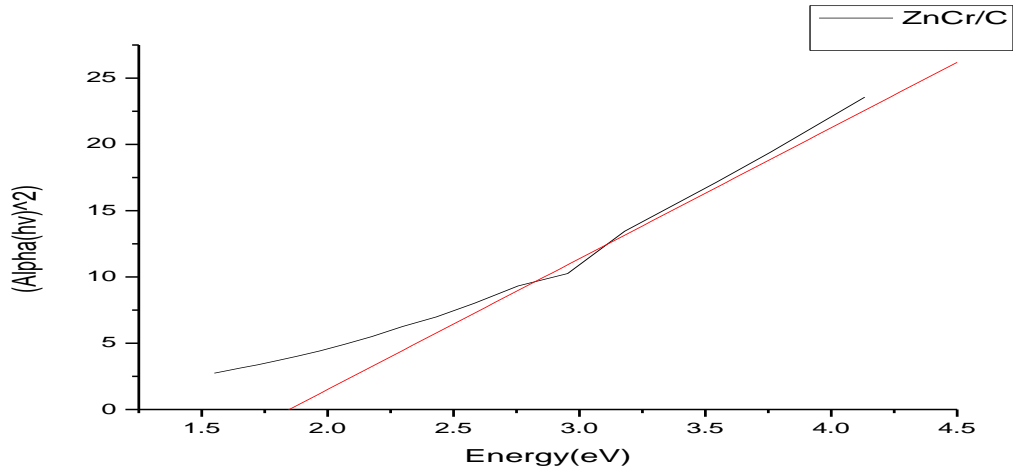
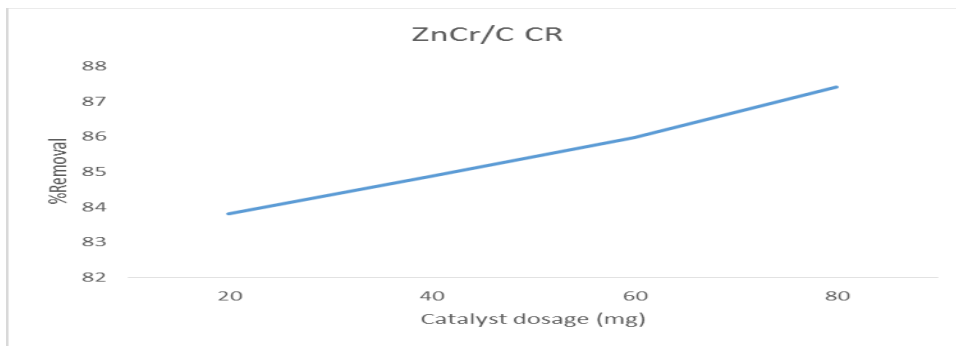


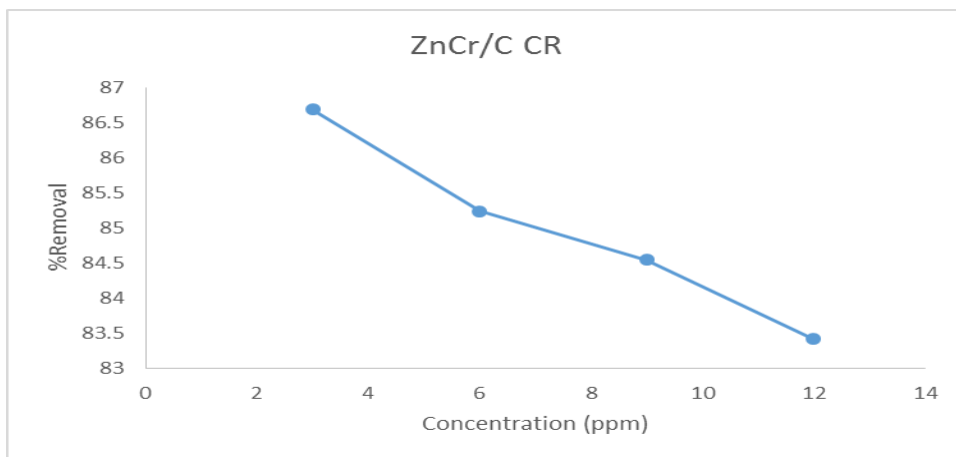
Figure 5: TGA profile of ZnCr/C



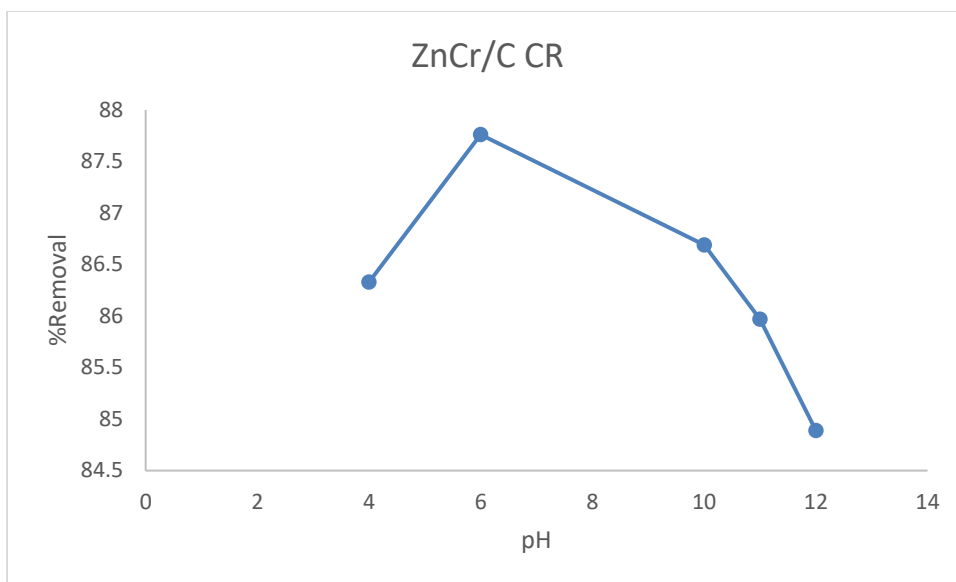
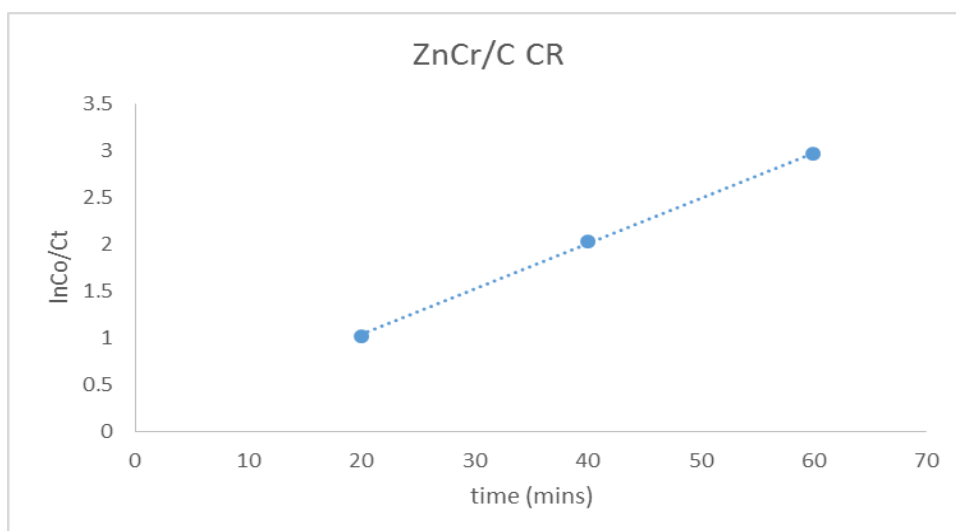
**Figure 6:** Tauc plot of ZnCr/C



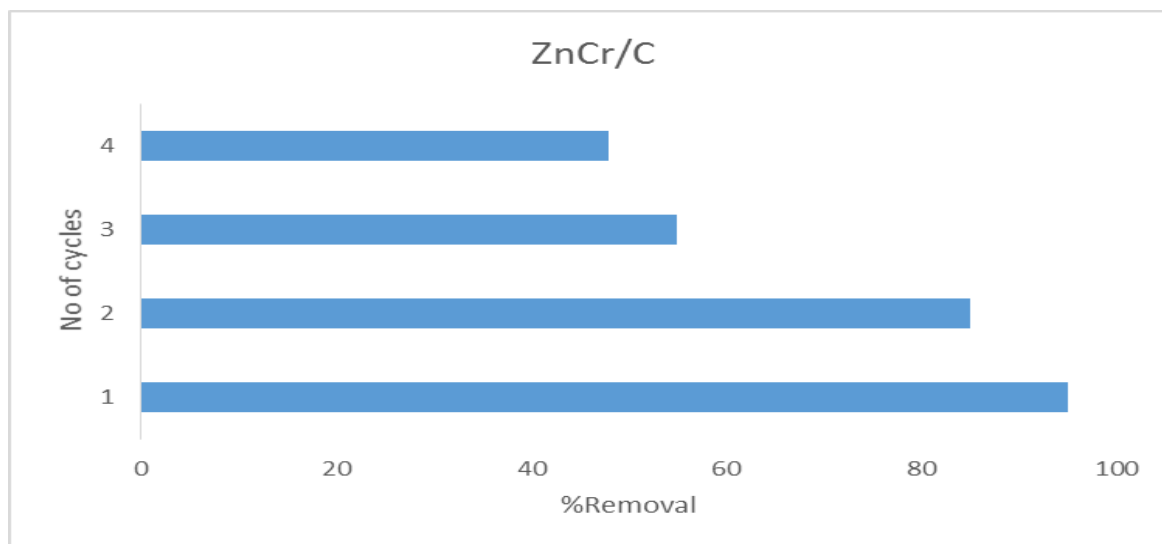
**Figure 7:** Effect of catalytic dosage



**Figure 8:** Effect of concentration

**Figure 9:** Effect of pH**Figure 10:** L-H kinetic model**Table 1:** Langmuir-Hinshelwood model parameters

LDH	Dye	Kapp (min <sup>-1</sup> )	Rate (molL <sup>-1</sup> min <sup>1</sup> )	R <sup>2</sup>	t <sub>1/2</sub> (mins)
ZnCr/C	CR	0.0361	2.166	0.9954	19



**Figure 11.** Recovery of ZnCr/C

## DISCUSSION

### Characterization of ZnCr/C

**Figure 1.** shows the XRD Pattern of ZnCr/C, sharp diffraction peaks located at  $2\theta = 26.1^\circ$ , and  $31.0^\circ$  for ZnCr/C are identified as diffraction planes of the LDH structure, which corresponds with the database of JCPDS number 38-0486. This confirmed the formation of the brucite-like LDH structure. The crystallite size is calculated to be 3.77nm. In **figure 2.** The morphology was investigated through SEM. The SEM image shows the sheet morphology Zn-Cr/C, in the catalyst small particles, are aggregated to form the sheet morphology. **Figure 3.** Shows EDS spectra of ZnCr/C which confirmed the C, O, Cr, Na, Cl and Zn elements in Zn-Cr/C-LDH. The EDS data reflects that the synthesized catalyst containing C, O, Cr, Na, Cl and Zn are present in 1.68, 0.09, 3.92, 23.9, 52.04 and 19.26 weight% respectively. **Figure 4.** Shows FTIR Spectra of ZnCr/C. the broadband at  $3286\text{cm}^{-3}$  represents the hydroxyl group vibrations, and a band at  $1354\text{cm}^{-1}$  corresponds to the vibration of chloride anions and  $1439\text{cm}^{-1}$  due to C-H

stretching. FTIR analysis exhibited sharp peaks at  $762\text{cm}^{-1}$  which were attributed to the M-O bond in the lattice structure of metals of Zn-Cr/C catalyst (Garzali and Muhammad, 2019). **Figure 5.** Shows the TGA profile of the ZnCr/C. The transition at  $100^\circ\text{C}$  corresponds to water loss. The LDH starts to dehydroxylate at  $300^\circ\text{C}$ . Another weight loss is observed between  $300^\circ\text{C}$  to  $500^\circ\text{C}$  due to the conversion of the LDH catalyst to LDO (Seftel *et al.*, 2008). **Figure 6** shows the tauc's plot, the band gap energy of 1.84eV for ZnCr/C suggests that the photocatalyst will work in the visible light range.

### Effect of Operational Parameters

Active sites of the LDH catalyst increase with increase in the catalytic dosage as shown in figure 7. High CR dye concentration causes the accumulation of dye molecule on the active sites of the catalyst which reduces the percentage of dye removal as shown in figure 8. CR anions compete with OH anions in alkaline medium therefore percentage removal is



high in the acidic medium as shown in figure 9 (Garzali and Muhammad, 2019).

### Photolysis and Photocatalytic Activity

The photolysis of CR dye under UV-Irradiation for one hour is 1.4% and the

### Kinetic Studies

The kinetics of CR dye degradation over the ZnCr/C photocatalyst was investigated. It illustrates the photocatalytic removal of dye as a function of irradiation time in the presence of different LDH which followed Langmuir–Hinshelwood model as shown in Equation 1.

$$R = -\frac{dC}{dt} = KrKc = KappC \quad (1)$$

where r is the rate of the reaction, Kr is the reaction rate constant, C is the concentration. under initial conditions of photocatalytic procedure, (t = 0, C = Co), it became Equation (2).

$$\ln \frac{Co}{Ct} = Kappt \quad (2)$$

Co was the initial concentration of dye and C was the concentration at a time 't'. the corresponding Kap

(Kinetic constant) (Bruna *et al.*, 2009), half-life parameters and regression relative coefficient values are given in Table 1

### Recyclability of the Catalyst

The recovery, reuse and durability of ZnCr/C photocatalyst are economical and eco-friendly. the LDH was recovered by centrifuging in water and ethanol mixture three times for complete cleaning of the LDH catalyst. Then the catalyst was dried at 75°C for 8 h and recycled for another cycle keeping the concentration of CR dye and the LDH constant. ZnCr/C shows a decrease from 95% to 85%. 55% and 48% in the second third and fourth cycles respectively.

### ACKNOWLEDGMENT

We acknowledged the Islamic Development bank for sponsoring this research work

photocatalytic activity of ZnCr/C on CR dye after one hour UV-Irradiation is 88.5%. This suggests that photocatalytic activity of ZnCr/C is the major cause of CR degradation and the effect of photolysis is negligible.

### CONCLUSION

The cheap and diverse morphology makes LDH a suitable candidate in the field of catalysis. Zn-Cr/C was synthesized through the co-precipitation method. SEM analysis shows that the catalyst was grown in nanosheet morphologies. FTIR and XRD analysis confirmed the formation of LDH nanostructure. The catalyst was effective in the de-colouration and mineralization of CR from the aqueous solution under ultraviolet conditions. The Zn-Cr/C-LDH showed good catalytic activity in all conditions and this is due to its lower band gap energy

### CONFLICT OF INTEREST

There was no complicit of interest between the authors.

## REFERENCES

- Ahmed, N. Morikawa, M. & Izumi, Y. (2011) Photocatalytic Conversion of CO<sub>2</sub> into Methanol using optimized Layered Double Hydroxide Catalysis. *Catal. Today* 185(1)263–269.
- Bruna, F. Celis, R. Pavlovic, I. Barriga, C. Cornejo, J. & Ulibarri, M. A. (2009) Layered Double Hydroxide as Adsorbents and Carriers of Herbicide (4-chloro-2-methylend Mg-Al-Feoxy) Acetic Acid (MCPA): Systems Mg-Al, Mg-Fe J. *Hazard. Mater.* 168 (1)1476–1481.
- Choy, J. Park, M. & Oh, J. (2016) Immobilization of Fructose-6-phosphate Aldolase in Layered Double Hydroxides. *Curr. Nanosci.* 2 (1) 275–281.
- Crisan, M. Braileanu, A. Crisan, D. Raileanu, M. Dragan, N. Mardare, D. Teodorescu, V. Ianculescu, A. Birjega, R. & Dumitru, R. (2008) Sintering of Nanocrystalline Metastable Alumina. *J Therm Anal Cal.* 92(1)7–13.
- Fujishima, A. Zhang, X. & Tryk, D. A. (2008) TiO<sub>2</sub> photocatalysis and related surfaces. *Surf Sci Rep.* 63:515–82.
- Garzali, F & Muhammad S. (2019) Degradation of Methyl Red Using Cd-Sb/C Layered Double Hydroxide *ChemSearch Journal.* 10(1)123 – 129
- Gomes C. Silva, Bouizi, Y. Fornes, V. & Garcia, H. (2009) Layered Double Hydroxide as Highly efficient Photocatalyst for Visible Light Oxygen Generation from Water. *J. Am. Chem. Soc.* 131(1)13833–13839.
- Guida, A. Lhouty, M. Tichit, D. Figueras, F. & Geneste, D. (1997) Hydrotalcites as Base Catalysts. Kinetics of Claisen-Schmidt Condensation, Intramolecular Condensation of Acetonyacetone and Synthesis of of Chalcone. *Appl. Catal. A.* 164 (1) 251–264.
- Gunjakar, J. L. Kim, T. W. Kim, H. Kim, L. & Hwang, J. (2011) Highly Active Visible Light Photocatalysts with improved Chemical Stability. *J. Am. Chem. Soc.* 133 (1) 14998–15007.
- Hadnadev, M. Ranogajec, J. Petrovic, S. Markov, S. Ducman, V. & Marinkovic-Neducin R. (2010) Design of Self-Cleaning TiO<sub>2</sub> Coating on Clay Roofing Tiles. *Philos Mag.* 90(22)2989–3002.
- Lee, Y. Choi, J. Jeon, H. K. Choi, J.W. Lee, J. & Kang, K. (2011) Titanium Embedded Layered Double Hydroxides as Highly Efficient Water oxidation Photocatalysts under Visible light. *Energy Environ. Sci.* 4(1)914–920.
- Mohapatra, L. Parida, K. M. & Satpathy, M. (2012) Molybdate/Tungstate Intercalated Oxo-Bridged Zn/Y LDH for Solar Light Induced Photodegradation of Organic Pollutants *J. Phys. Chem. C.* 116 (1)13063–13070.
- Mousty, C. & Leroux, F. (2013) Co/Al Layered Double Hydroxides Nanostructures. *Recent Pat. Nanotechnol.* 6 (1) 174–192.
- Parida K. M & Mohapatra, L. (2012) Carbonate Intercalated Zn/Fe Layered Double Hydroxide. *Chemical Engineering Journal.* 179(1)131– 139.
- Seftel, EM. Popovici, A. Mertnes, M. De, K. Witte, G. & Tendeloo, V. (2008) Removal of Methylene Orange from Aqueous Solutions by Using Zn-Al Layered Double Hydroxide *Micropor Mesopor Mater.* 113(1)296–304
- Sivalingham, G. Nagaveni, K. Hegde, M. S. & Madras, G. (2003) Thermal and photocatalytic Behavior of Ti/LDH Nanocomposites. *Appl Catal B Environ.* 45(1)23–38.
- Teramura, K. Iguchi, S. Mizuno, Y. Shishido, T. & Tanaka, T. (2012) Insights into The Photocatalytic activity of ZnCr-CO<sub>3</sub> and Derived Mixed Oxides. *Chem. Int. Ed.* 51(1) 8008–8011, S8008/8001–S8008/8009
- Zhao, Y. Chen, P. Zhang, B. Zhang, S. Tian, L. Lu, J. Li, Z. Cao, X. Wang, B. Wei, M. Evans, D. G. & Duan, X. (2012) Highly

Dispersed  $\text{TiO}_6$  Units in a Layered  
Double Hydroxide for Water Splitting.  
*Chem. Eur. J.* 18(1)11949–11958.