Research Article

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

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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 2Θ 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 (Hnadadjev 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 \( \text{H}_2\text{O} \) and \( \text{OH}^- \) to generate \( \text{OH} \) 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, Gunjakar 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\(_3\) and ZnCl\(_2\) were mixed in a 1:3 molar ratio. Prior to mixing, 250 cm\(^3\) of 0.1M CrCl\(_3\) was mixed with 250 cm\(^3\) of 0.3M ZnCl\(_2\) in 1000 cm\(^3\) 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\(_3\)H\(_7\)OH: H\(_2\)O mixture (8:2). The product was then dried overnight in an oven at 53\(^\circ\)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).

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 10cm³ 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

<table>
<thead>
<tr>
<th>LDH</th>
<th>Dye</th>
<th>Kapp (min(^{-1}))</th>
<th>Rate (molL(^{-1})min(^{-1}))</th>
<th>R(^2)</th>
<th>t(_{1/2}) (mins)</th>
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<tr>
<td>ZnCr/C</td>
<td>CR</td>
<td>0.0361</td>
<td>2.166</td>
<td>0.9954</td>
<td>19</td>
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</table>
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 3286cm$^{-1}$ represents the hydroxyl group vibrations, and a band at 1354 cm$^{-1}$ corresponds to the vibration of chloride anions and 1439 cm$^{-1}$ due to C–H stretching. FTIR analysis exhibited sharp peaks at 762cm-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°C corresponds to water loss. The LDH starts to dehydroxylate at 300oC. Another weight loss is observed between 300°C to 500°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 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.

**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.

\[
R = -\frac{dc}{dt} = KrKc = KappC
\]

(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).

\[
\ln \frac{Co}{Ct} = Kappt
\]

(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.

**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

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**CONFLICT OF INTEREST**

There was no complicit of interest between the authors.
REFERENCES


