



ZnCr/C Layered Double Hydroxide: Synthesis, Characterization and Photocatalytic Application on Methylene Blue Removal

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ABSTRACT

In this paper, ZnCr/C-layered double hydroxide (LDH) photocatalyst was successfully prepared using co-precipitation method. The catalyst was characterized using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy dispersive spectroscopy (EDS), Fourier transformed infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), and band gap energy determination. The XRD spectra showed 11.9°, 26.1° and 31.0° at 2 θ which confirmed the formation of ZnCr/C LDH. Band gap energy of the photocatalyst was determined to be 1.84eV which indicated that the photocatalyst was visible in the UV-visible region. The efficiency of the photocatalyst in the photodegradation of methylene blue (MB) was investigated. The kinetics of the photodegradation of MB in aqueous solution was observed to obey the Langmuir-Hinshelwood model. The catalyst showed an excellent recyclability and durability.

ARTICLE INFO

Keywords:

UV-light
Photocatalyst
LDH
MB
Activated Carbon

Received: 12-08-2021

Accepted: 16-11-2021

ISSN: 2651-3080

DOI: 10.54565/jphcfum.981503

Introduction

Industrial waste water contains many hazardous and non-biodegradable chemicals including dyes. These are toxic to environmental and human life causing many carcinogenic and mutagenic complications. Removing these dyes from waste water became necessary. [1]

It is vital to develop economical and effective technologies for the removal of MB from wastewater. Typical methods to deal with MB-contaminated wastewater are adsorption [2], microbial degradation [3], hydroxyl-radical advanced oxidation [4], and photocatalytic process [5]. Regarding such methods, the photocatalytic method shows a high MB removal capacity from wastewater. The Advanced oxidation process is a kind of oxidation technology that can oxidize organic pollutants in wastewater and decompose them into water and carbon dioxide, with high mineralization. Photocatalytic oxidation, because of its low toxicity, high effectiveness, and eco-friendly properties, has had a high impact in the field of wastewater treatment. Although TiO₂ [6] and ZnO [7] are commonly used photocatalysts in photocatalytic technology, their band gap energies are too wide to generate active species for contaminant removal

under UV-light irradiation [8]. Layered double hydroxides (LDHs) or hydrotalcite-like compounds have anion-exchanging lamellar galleries, consisting of positive charge metal hydroxide layers and anions in the interlayer [9]. LDH has high removal efficiency of dyes because of its weak interlayer hydrogen bond. They have high surface area, excellent thermal stability and excellent anionic exchange capacity. [10]

In this work, novel ZnCr/C-LDH was synthesized using carbon black which was a petroleum by product, will be used to remove MB from aqueous solution.

Materials and Methods

Preparation of Activated Carbon

Activated carbon was prepared using thermal method, by heating carbon black at 400°C for 30 minutes. This method was patented by Teng et al. [11]

Synthesis of Zn-Cr/C-LDH

ZnCl₂ and CrCl₃ were dissolved in ratio 1:3 thoroughly in distilled water. To this reaction mixture, 10 wt% of activated

carbon was dispersed by continuous stirring with the help of magnetic stirrer. To this mixture freshly prepared 0.1 M NaOH solution was added and continuously monitored till pH 9. After this, the suspension was allowed to age on a hot plate for 6 h at 60°C with homogenous stirring. After aging, the surplus solution was removed and the precipitate was washed three times with C₂H₅OH: H₂O mixture (8:2). The derived product was dried in an oven overnight at 50 °C and stored in clean tube for further characterization.

Characterization

The crystallographic structure of the LDH was achieved by X-ray diffraction (XRD) analysis. This is done by irradiating the LDH with incident X-rays and then measuring the intensity and scattering angle of X-ray that are scattered by Zn-Cr/C layered double hydroxide. The XRD data was analyzed using Full Proof Suite 3.0.

The surface morphology of the LDH was achieved by using Scanning electron microscopic (SEM) analysis. SEM shows the morphology of Zn-Cr/C LDH catalyst. EDS was used to determine the elemental constituents of ZnCr/C. Both SEM and EDS were carried out using the same machine (JEOL JEM-2010). Qualitative analysis of the main functional groups that are present in the LDH was determined with a FT-IR spectrophotometer. FTIR-Cary 630 from Agilent technologies was used and the spectra were recorded in the wavelength interval 4000 to 750 cm⁻¹. The band gap energy was determined using UV-Visible spectroscopy Perkin Elmer Lambda 35. TGA analysis was conducted using TGA machine (agilent technologies),

Photocatalytic Experiment

Exactly 80mg of Zn-Cr/C was dispersed in 30cm³ of 3ppm MB dye solution. The above suspension was magnetically stirred for 40mins in the dark to obtained adsorption-desorption equilibrium. The mixture was then irradiated using 50Hz UV lamp at 365nm. A 10cm³ aliquot was taken at 20mins interval, centrifuged at 270rpm and filtered prior to absorbance measurement [12]. The percentage removal efficiency R.E. (%) of each catalyst was evaluated by using the following equation.

$$R.E (\%) = \frac{C_0 - C_t}{C_t} \times 100 = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

C₀ represents the initial concentration of MB dye solution at time = 0, C_t is the concentration of dye solution after some

time = t. A₀ represent the absorbance of the initial concentration of the dye solution at time = 0 and at is the absorbance of dye solution at time = t

Results and Discussion

Characterization

ZnCr/C-LDH was characterized using X-ray Diffraction (XRD), Scanning electron Microscopy (SEM), energy dispersive spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FT-IR), band gap determination and Thermo gravimetric analysis (TGA).

XRD suggest that the 2θ values at 11.9° for ZnCr/C confirms the formation of a brucite-like LDH structure as shown in figure 2. The peaks at 26.1°, 31.0° further suggest the LDH nature of ZnCr/C. XRD pattern propose the presence of chloride anions in the inner gallery of the LDH. [13]

SEM image in figure 3 shows the LDH consist of mixed particle which form the catalyst nanosheet morphology, the particles grown on sheet which aggregate to form the LDH structure. EDS in figure 4 confirmed the present of Zn, Cr, Cl, C and O in the LDH nanostructure. C, O, Cr, Na, Cl and Zn correspond to 1.67, 0.09, 3.91, 22.9, 53.04 and 19.26 weight%.

FTIR as shown in figure 5 recorded OH vibration at band 3286cm⁻³, a chloride anions vibration at 1354 cm⁻¹ 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 LDH. [14]

The band gap energy of ZnCr/C catalyst was determine using the Tauc Plot Method. The expression proposed by Tauc, Davis and Mott were used

$$(h\nu\alpha)^{1/n} = A(h\nu - E_g) \quad (2)$$

Where: h: Plank's constant=6.623×10⁻³⁴Js, v: frequency of vibration, α: absorption coefficient, E_g: band gap, A proportional constant. Eg value was calculated to be 1.84eV. this suggest that the photocatalyst is visible in the UV-Visible region. [15]

TGA in figure 6 shows water loss at 100°C. The thermal stability of the lamellar gallery reduced and start to dehydroxylate at 300°C and there was a conversion of the LDH catalyst to LDO between 300°C to 500°C [16]

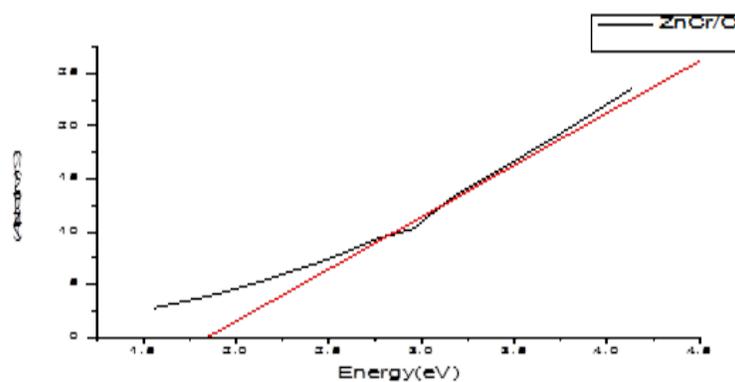


Figure 1. Tauc plot of ZnCr/C

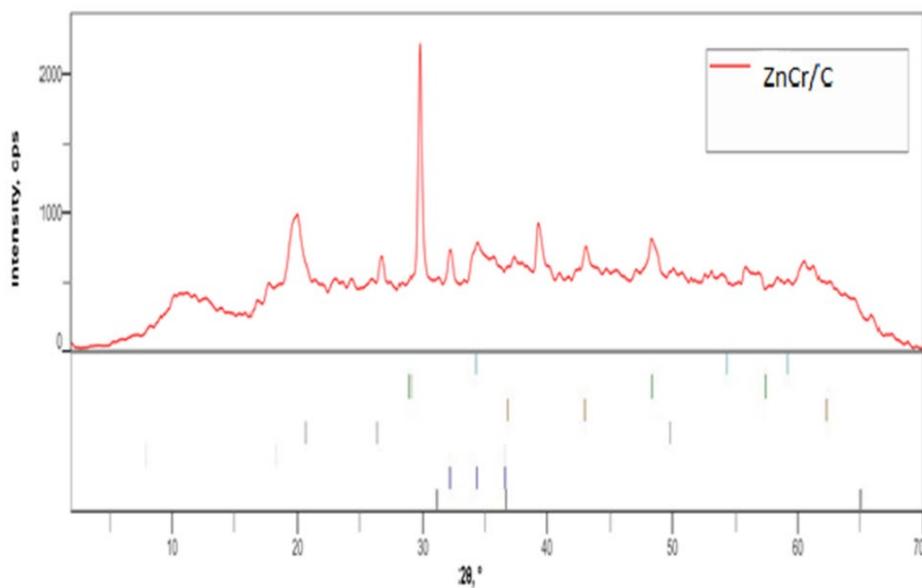


Figure 2. XRD pattern of ZnCr/C

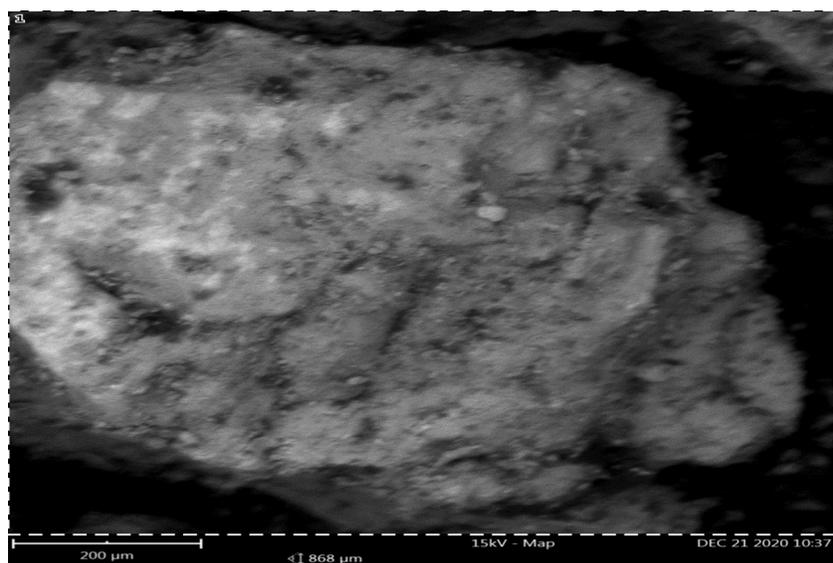


Figure 3. SEM image of ZnCr/C

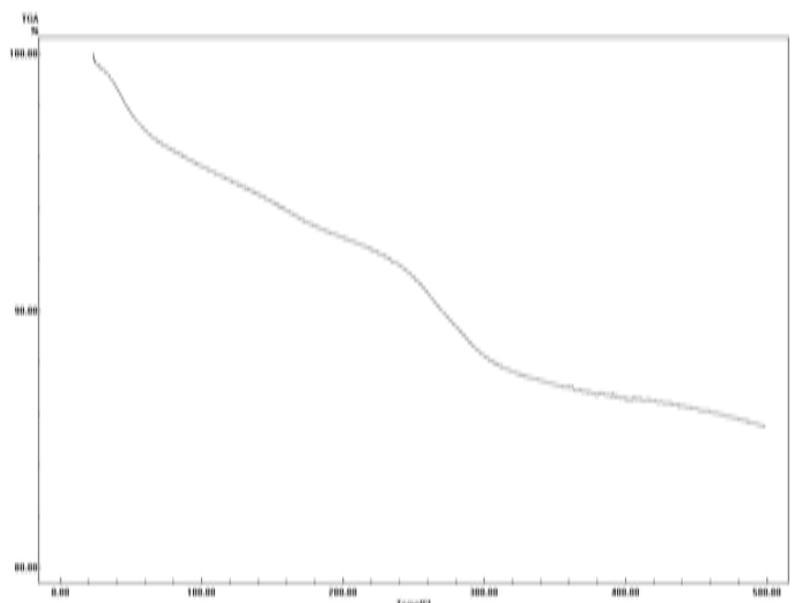


Figure 6. TGA profile of ZnCr/C

Optimization

High MB dye concentration causes the accumulation of dyes on the active site, this reduces the percentage removal by blocking the direct interaction of the UV light and the active

sites. H^+ in acidic medium compete with MB cations which reduces percentage removal hence high removal is observed in alkaline medium. Increase in amount of LDH cause increase on dye removal because of increase in active site [17]

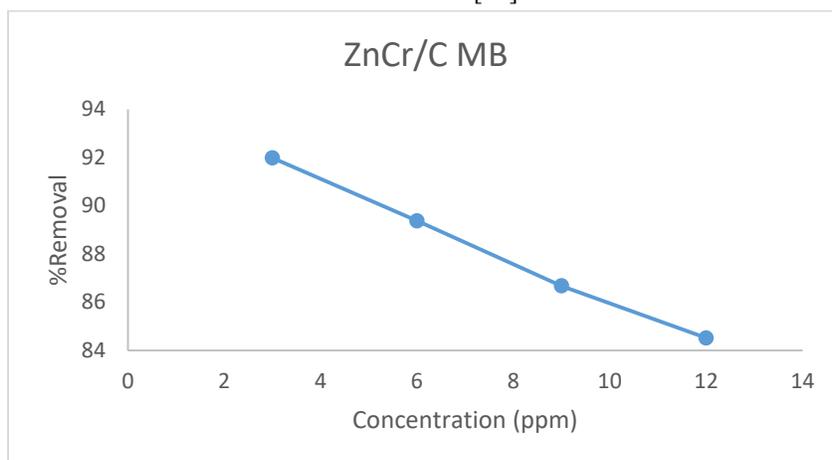


Figure 7. Effect of MB concentration

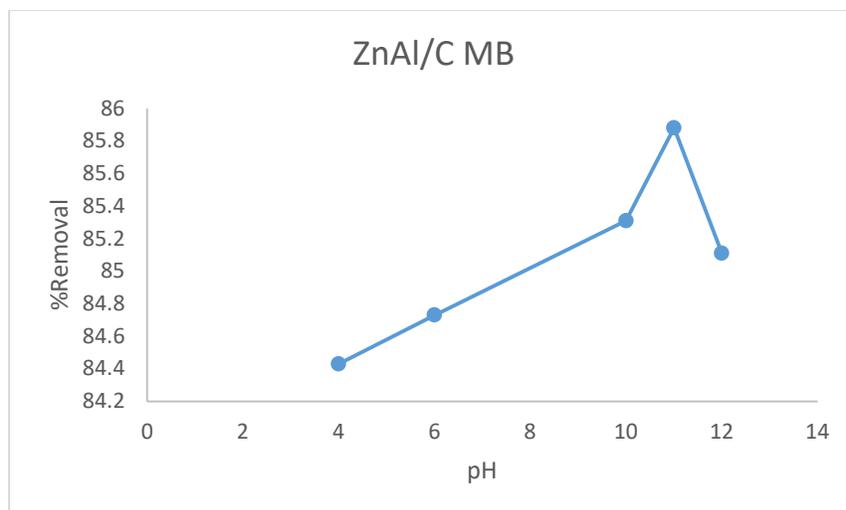


Figure 8. Effect of pH

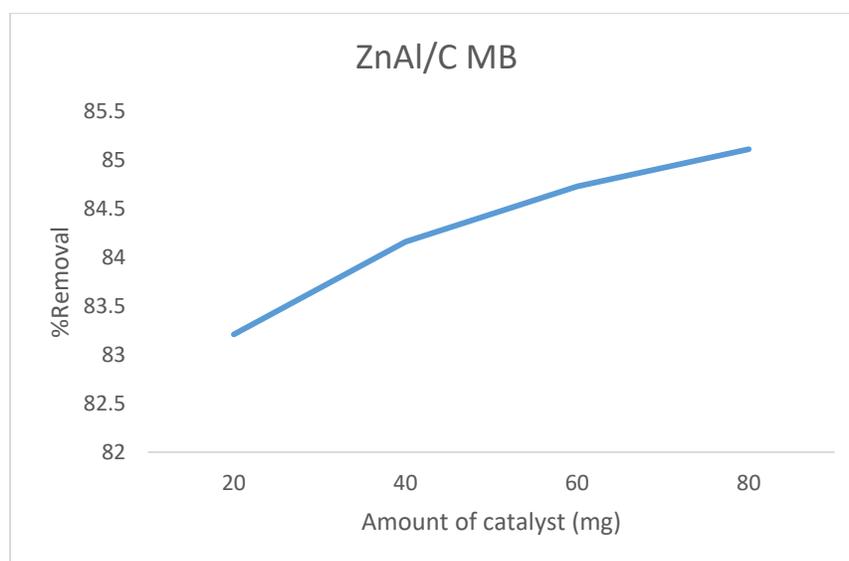


Figure 9. Effect Of ZnCr/C Amount

Photocatalytic Application

MB degradation under 1hr UV-light was 0.8%. The photocatalytic activity of ZnCr/C on MB was 95%. This shows that the effect of photolysis is negligible.

Kinetic Studies

The kinetics was investigated by using eq. (3)

$$\ln C_0/C = K_{app}t \quad (3)$$

C_0 was the initial concentration of dye and C was the concentration at time ' t '. the rate is $2.994 \text{ (molL}^{-1}\text{min}^{-1}\text{)}$ and the half-life is 13mins.

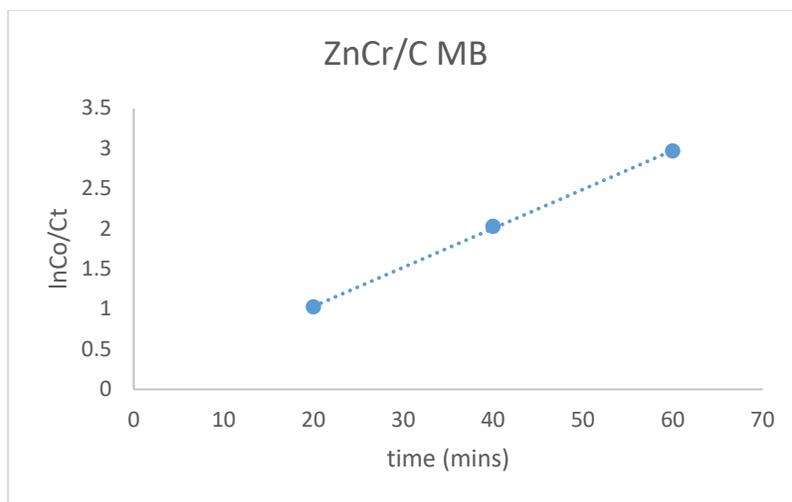


Figure 10. L-H model

Regeneration and Reuse

The reuse, regeneration and stability of a novel photocatalyst had significant impact on the removal process, hence made the application of the materials more economical. The Catalyst was regenerated by centrifuging and washing with

ethanol and water. The suspension was filtered, precipitate was dried in an oven for 6hrs at 70°C. ZnCr/C shows decrease from 95% to 85%, 55% and 48% in the second, third and fourth cycles respectively. Even after four cycles, the results show stability and durability of the LDH

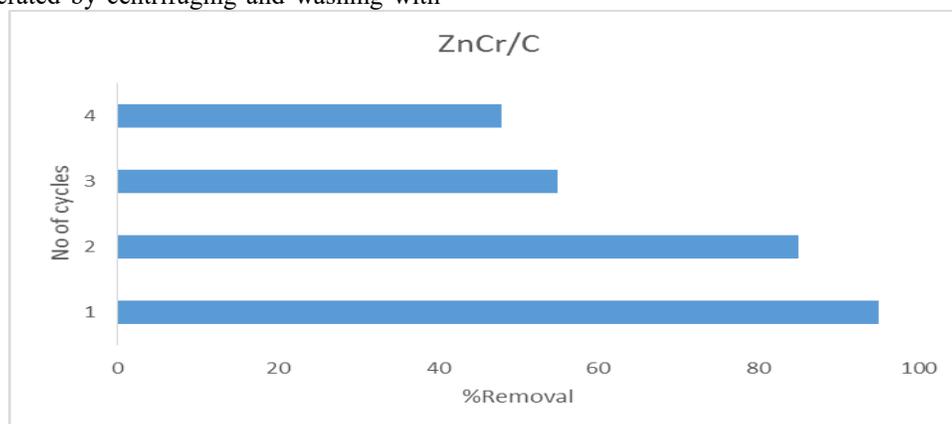


Figure 11. Reusability of ZnCr/C

Conclusion

ZnCr/C was synthesized and characterized using FTIR, SEM, EDS and XRD, TGA and band gap. Photocatalytic experiment reveals 95% MB removal by ZnCr/C. Langmuir-Hinshelwood model shows the kinetics of the photodegradation of the photocatalytic reaction as pseudo first order. The photocatalyst was still active even after the fourth cycle indicating its durability and stability. Eco-friendly LDH photocatalyst offers a promising effectiveness for MB dye removal.

Acknowledgment

Thank you, the Islamic development bank, for your financial support.

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