ORIGINAL RESEARCH PAPER

Mg-Al LDH and Calcined LDH: Green Nanocatalysts for wet peroxide oxidation of phenol in wastewater

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ABSTRACT

The catalytic wet peroxide oxidation (CWPO) of phenol from wastewater using Mg-Al LDH and calcined LDH at 500 ºC was investigated. The LDH was synthesized by co-precipitation and was characterized by XRD, FTIR, SEM, EDS, and BET. XRD results indicated that during the calcination of LDH at 500 ºC, LDH decomposed to the mixed oxide. The SEM images approved Mg-Al LDH comprised of flakes and the calcined LDH comprised of spherical nanoparticles. BET results indicated the specific surface area of 100.2 and 86.3 m2.g-1 for pure LDH and calcined LDH, respectively. The process was optimized by one factor at a time method and considering four process factors i.e. reaction temperature, peroxide dosage, initial phenol concentration, and reaction time. The optimum conditions resulted at initial phenol concentration of 100 ppm, reaction temperature of 60 ºC, with peroxide volume of 3 mL and time on stream of 45 min over calcined LDH with maximum 85% removal of phenol. On the pure LDH, the maximum phenol removal (79%) resulted in a peroxide volume of 2.5 mL at 55 min. The study concluded that the calcined Mg-Al LDH due to the synergistic effect of MgO and Mg-Al mixed oxide showed higher catalytic activity despite a relatively low surface area.

Keywords: *Mg-Al LDH, phenol, wet peroxide oxidation, mixed metal oxide, optimization.*

INTRODUCTION

Phenol and phenolic compounds are released from various industries such as petrochemical and coking processes [1, 2]. It is rapidly absorbed through the skin and by inhalation through the lungs. Upon absorption of moderate amounts of phenol, it is detoxified by conjugation with sulfuric and glucuronic acids and excreted in the urine. High exposures to phenol may be fatal to human beings; infants appear to be hyper susceptible to phenol. Although phenol is a tumor promoter, it is not a carcinogen, cocarcinogen, or teratogen and, most probably, is not a mutagen [3]. The biological degradation of phenol is hard and it is very toxic so it is necessary to reduce the amount of phenol from wastewater. Conventional methods have been applied such as steam distillation, liquid-liquid extraction, adsorption, solid-phase extraction, wet air oxidation, catalytic wet air oxidation, and biodegradation for removal of phenols. Advanced technologies for the removal of phenols include electrochemical oxidation, photo-oxidation, ozonation, UV/H_2O_2, Fenton reaction, membrane processes, and enzymatic treatment [3-5]. The main advantages of advanced oxidation processes are the oxidation is usually complete and phenol is degraded to carbon dioxide and water under mild conditions.

Among the advanced oxidation processes (AOP), catalytic wet peroxide oxidation (CWPO) is recognized as a low-cost technology [1-5], since

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it operates with simple equipment and under mild conditions (e.g., at atmospheric pressure and low temperatures. So, it is a suitable method for phenol remediation. Through the various methods used for the removal of the phenol, its catalytic oxidation by hydrogen peroxide is considered a suitable method. The complete degradation of phenol has resulted from this method at lower temperatures [1-2]. Like other catalytic processes, the property of the catalyst affects the efficiency of the process. Recently the use of transition metal catalysts especially, the catalysts containing iron and copper has been reported [6-7].

Layered double hydroxides (LDHs) are the materials containing two cationic layers with a positive charge, then an anionic interlayer (CO_3^{2-}, NO_3^{2-}, Cl^- etc) is placed between layers with water molecules and stabilized the structure. [1, 6]. General chemical formula of LDH is $[M^{2+}_{1-x} M^{3+}_{x} (OH)_2]^{x+} (A^{n-})^{x/n} \cdot m H_2O$. In this formula, M^{2+} is divalent cation like Fe^{2+}, Mg^{2+}, Ni^{2+}, Cu^{2+}, and M^{3+} is trivalent cation like Al^{3+}, Cr^{3+}, Ga^{3+} and etc [8-13]. These materials have a wide surface area and the perfect ability for ion exchange. This ability turns LDHs as a good catalyst for eliminating harmful compounds in wastewater like oxo methylate, chromate, etc LDH has different applications such as adsorbents of aqueous pollutants [7-13].

The present work aimed to develop the MgAl LDH and calcined LDH as the catalyst in the oxidation of phenol from simulated wastewater by the catalytic wet peroxide oxidation process and to compare the activity of pure LDH with that of nanocomposite resulted from calcination. The samples were characterized by XRD, FTIR, SEM, EDS, and BET. The process parameters such as phenol concentration, reaction temperature, peroxide dosage, and time on stream were considered to optimize the CWPO process.

EXPERIMENTAL

Synthesis of Mg-Al LDHs

The materials used in the synthesis were $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, Na_2CO_3, and NaOH which all were supplied from Merck company (Germany).

The Mg-Al LDHs (molar ratios Mg/Al = 2) were prepared by co-precipitation of magnesium and aluminum salts from a homogeneous solution. A typical synthetic procedure is as follows: 6.4 g $Mg(NO_3)_2 \cdot 6H_2O$ and 4.6 g $Al(NO_3)_3 \cdot 9H_2O$ dissolved in 100 ml of deionized water under vigorous

stirring. After 10 min, solution B containing 1.125 g Na_2CO_3 and 4 g NaOH were added dropwise in the above homogenous solution until pH reached 9.5-10. The mixture solution was kept under constant magnetic stirring for 3 min at room temperature. Then the solid was separated by a vacuum filter and washed thoroughly with water and finally dried overnight at 70 ºC. To prepare the calcined LDH, the Mg-Al LDH sample was thermally treated at 500 ºC for 3h.

Characterization of catalyst

The crystalline phases of catalyst were investigated by a Philips PW1800 diffractometer and Cu K_α radiation (λ= 1.54 ˚A). Fourier transform infrared (FT-IR) spectra were recorded on a Bruker spectrometer (model TENSOR 27) at room temperature using KBr disc technique.

The morphology of the mixed oxides was determined via scanning electron microscopy (SEM) by a MIRA3 TESCAN instrument equipped to EDS analysis with precoating samples with gold. The specific surface area of the nanocatalyst was determined using the BET method. The N_2 adsorption-desorption isotherms were carried out using Belsorp, Japan.

Experimental process

A batch reactor was used to test the catalytic wet oxidation. In all studies, the catalyst dosage and stirring rate (500 rpm) were kept fixed. To optimize the process, the different values of hydrogen peroxide, reaction time, reaction temperature, and phenol initial concentration were considered. The concentration of the remained phenol after the reaction was detected and measured by a UV-Vis spectrophotometer (PG Instrument 80). The COD (dichromatic closed reflux method) was measured according to the standard methods book [14].

The percentages of phenol and COD removed were calculated using the following equation (Eq. 1):

$$R = \frac{[input] - [output]}{[input]} \times 100 \qquad (1)$$

Each test was repeated three times and the average value was reported. The RSD of the values was around 1%.

RESULTS AND DISCUSSIONS

sample characterization

Fig. 1 represents XRD patterns of Mg-Al–CO_3

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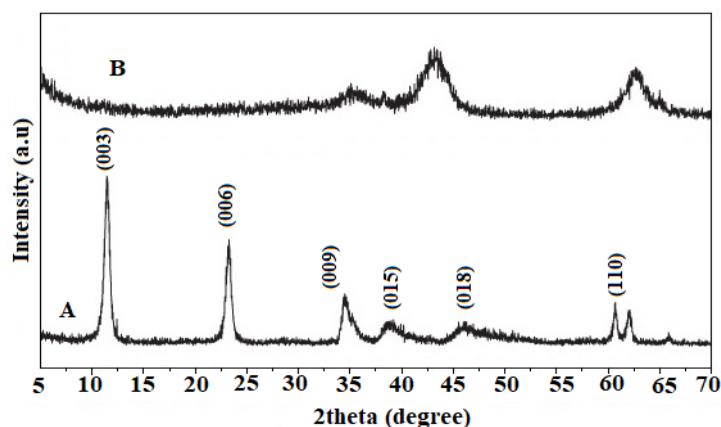
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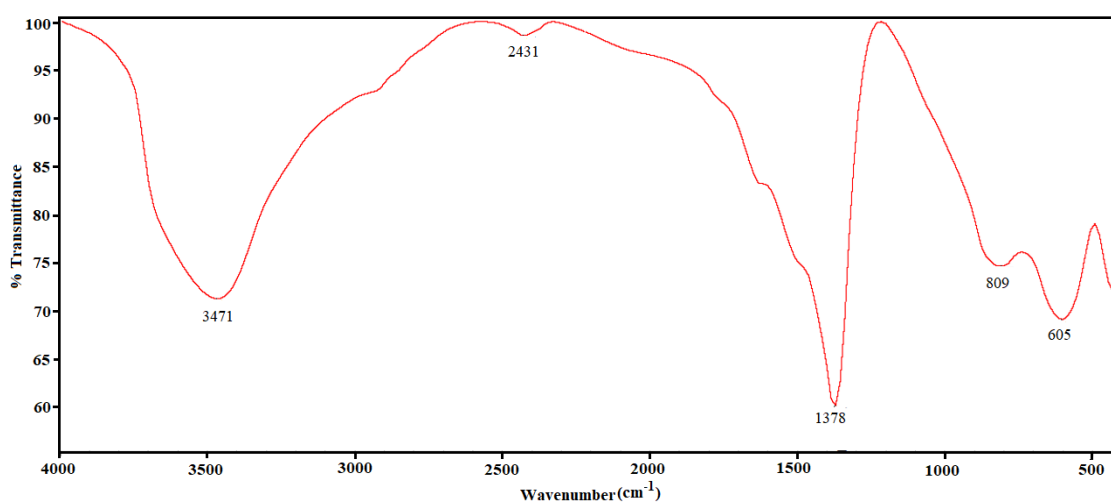Fig.1. The XRD patterns of Mg-Al LDH (A) and calcined LDH (B).

Fig.2. FTIR spectra of Mg-Al layered double hydroxide.

LDHs and calcined LDH. The patterns of Mg-Al–CO_3 exhibit the characteristic reflections of the hydrotalcite structure with a hexagonal lattice and R3m rhombohedral space group symmetry, further indicating the successful formation of the LDHs structure. The characteristic miller index of (003), (006), (009), (015), (018), and (110) as the main peaks of LDH structure are shown in the XRD pattern of the Mg-Al sample (Fig.1a). The XRD patterns of calcined LDH showed the disappearance of the peaks of hydrotalcite, due to the collapse of the structure of Mg-Al–CO_3 LDHs, and the appearance of broad peaks attributed to the formation of Mg-Al mixed oxides. This means that Mg-Al–CO_3 LDHs decompose into magnesium and aluminum oxides when heated at 500 °C. The broad peak at 40-45° corresponds to periclase (MgO)

(JCPDS Card No. 45- 946) [15]. It is reported in the literature that some Mg/Al double hydroxides, such as $Mg_2Al(OH)_7$ and $Mg_4Al_2(OH)_{14}.3H_2O$, decomposed to crystalline spinel and periclase (MgO) at temperatures as low as 400 to 500 º [15]. However, the spinel phase was not observed in pattern 3.b, which may indicate that complete dissolution of MgO from the hydrotalcite has not yet been achieved.

Fig. 2 shows the FT-IR spectrum of Mg-AL layered double hydroxides synthesized using the co-precipitation method. The peaks under 1000 cm^{-1} are because of the Mg-O and Al-O bond vibration and stretching. Naturally, peaks in 1377 and 3471 cm^{-1} are related to the existence of CO_3^{2-} and hydroxyls groups adsorbed to the layers, respectively. Besides, The broadband at 3471 cm^{-1}
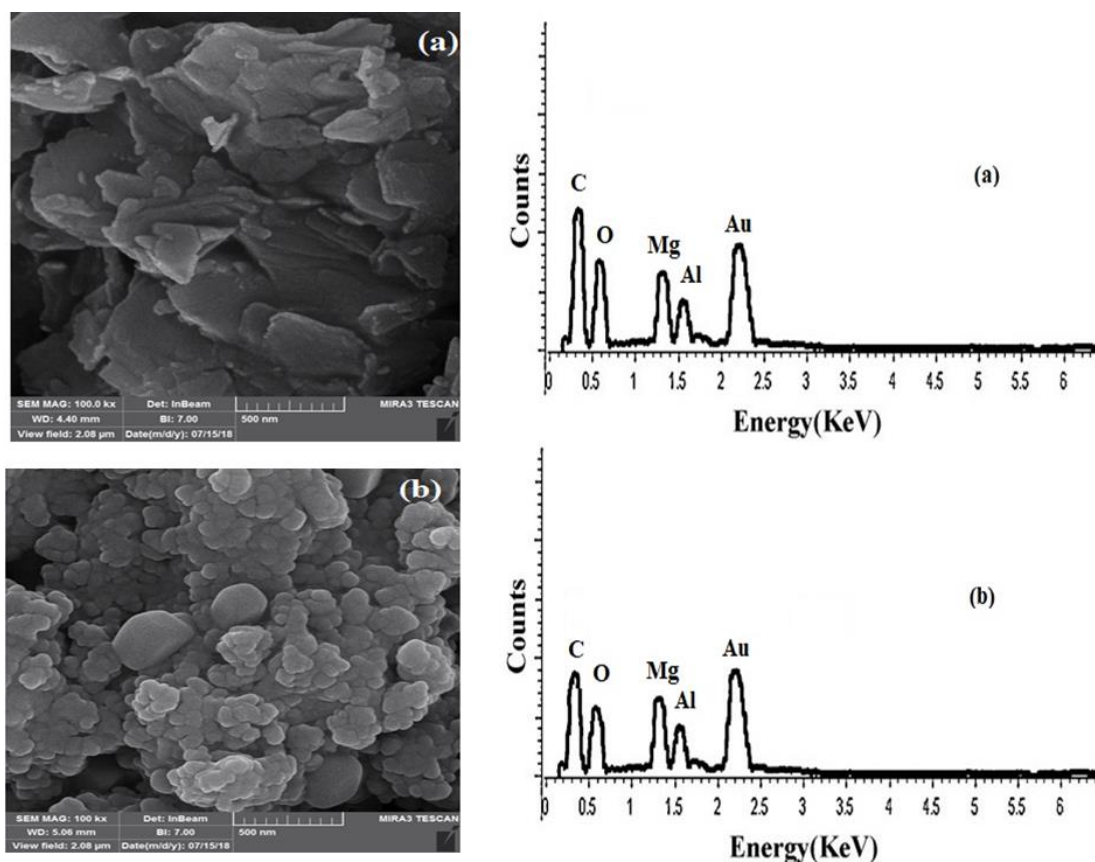
Fig.3. SEM images and corresponding EDS spectrum of (a) Mg-Al–CO$_3$ LDHs, (b) Mg-Al–CO$_3$ LDHs calcined at 500 °C.

is attributed to the hydroxyl groups of the LDH structure [2].

The particle morphology and chemical composition of the Mg-Al–CO$_3$ LDHs and calcined LDH can be seen in the SEM images presented in Fig. 3. The SEM image of Mg-Al–CO$_3$ LDHs (Fig.3a) showed a layered structure and particle aggregation with lateral size 50–100 nm. The SEM micrograph of the calcined LDH (3.b) revealed the collapsed layer structure, which further indicated the Mg-Al–CO$_3$ LDHs transforms into mixed magnesium and aluminum oxides. Also, the comparison of the EDS of MgAl LDH and calcined MgAl LDH showed that the intensity of peaks C and O for the calcined sample reduced to those of LDH, indicating the releasing or decomposing CO$_3^{2-}$ during the calcination. Besides, the mole ratio of Mg/Al is around 2, which is in agreement with the that used for the synthesis of LDHs.

The N$_2$ adsorption-desorption curves over the samples are shown in Fig.4. The curves follow from type III isotherm, indicating mesoporous materials. The average pore size and pore volume of MgAl LDH were 23 nm and 0.49 cm^3.g^{-1}, whereas The average pore size and pore volume of MgAl LDH were determined 21 nm and 0.46 cm^3.g^{-1}. According to BET analysis, the specific surface area of the LDH and calcined LDH were 100.2 and 86.3 m^2.g^{-1}, respectively.

Process optimization

The main process factors were considered in the optimization by one factor at a time method. In this method of optimization, at each time, one factor is optimized and the value of other factors is constant. First, the value of reaction temperature was optimized. The results are shown in Fig.5. To find the optimum temperature for the reaction, the reaction was performed at different temperatures. According to Fig.5, the optimum temperature for phenol removal over the Mg-Al LDH and the calcined LDH was 60 °C, which was applied in all tests. Bagheri et al [1] reported the optimum temperature of 50 °C for phenol degradation over
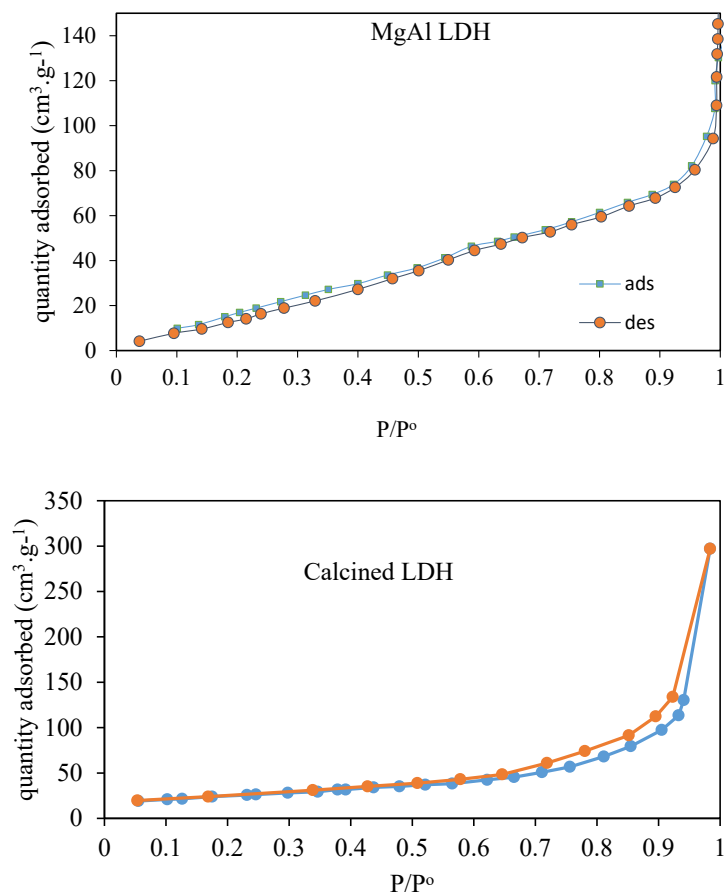
Fig.4. adsorption-desorption curves for N_2 over MgAl LDH and calcined LDH.
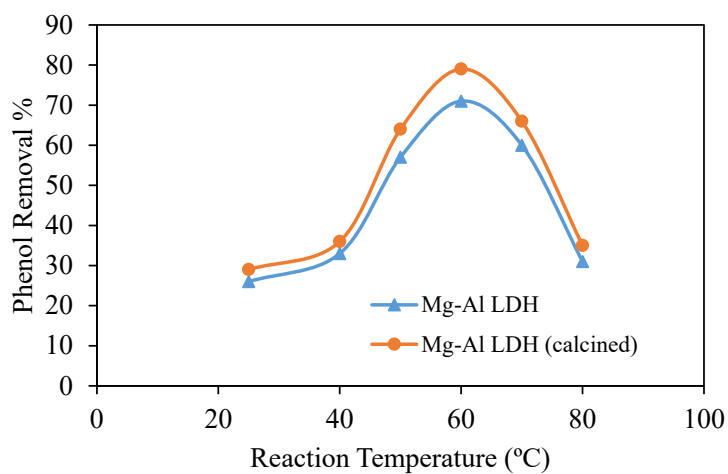

Fig.5. The removal of phenol at different reaction temperatures (reaction conditions: V = 100 mL, m = 0.05 g, initial phenol concentration: 100 mg L^{-1}, reaction time = 45 min).

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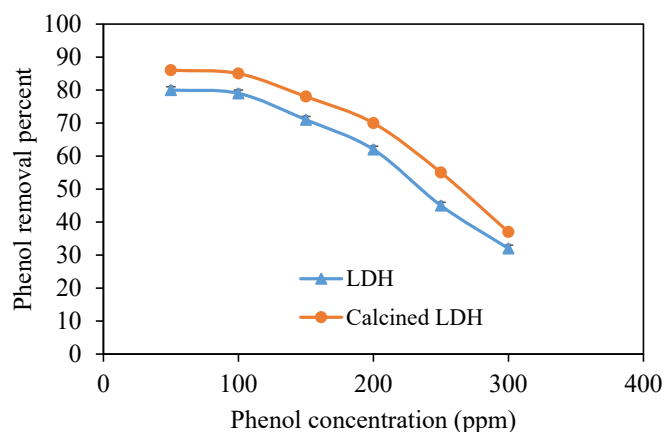
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Fig.6. Effect of concentration of phenol on its removal percentage in CWPO process on Mg-Al LDH and calcined LDH (reaction conditions: V = 100 mL, m = 0.05 g, reaction time = 45 min, temperature = 60 ºC).
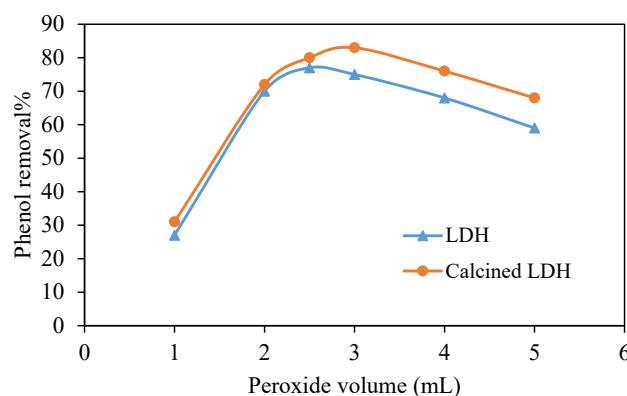

Fig.7. The effect of peroxide volume on phenol removal % over Mg-Al LDH and calcined LDH (reaction conditions: V = 100 mL, m = 0.05 g, initial phenol concentration: 100 mg L^{-1} , reaction time = 45 min, temperature = 60 ºC).

$CuCo_2$ and $CuMn_2$ spinel oxides.

Hosseini et al. investigated the catalytic wet peroxide oxidation of phenol solutions over $ZnFe_2O_4$ nano spinel at 70 °C [16]. Son et.al. reported the temperature of 90 °C as the optimum temperature at catalytic wet peroxide oxidation of phenol over Fe–Mn binary oxides diatomite composite [17]. It results that the activation energy for phenol oxidation over various catalysts differs together and depends on the catalyst type.

The second factor for optimization was the initial concentration of phenol in wastewater. The study was conducted at a concentration range of 50-300 ppm. The results as shown in Fig.6 indicates that the optimum concentration in this study was 100 ppm. Because above this concentration the phenol removal percentage reduced. So this concentration was applied at all tests. According to the Collision theory, the collision of the reactants increases with the increase of concentration of reactants. Besides, just the molecules with suitable energy i.e. activation energy could react together. Increasing the temperature provides the activation energy of the reaction. So, like every chemical reaction, these two factors are the most effective factors of the reaction.

The volume of the hydrogen peroxide was another factor that was optimized in the study.

For each catalyst, five tests were accomplished with different loadings of H_2O_2 and the results are presented in Fig.7. There is an optimum value for peroxide volume in that the 2.5 mL and 3 mL for the reaction over Mg-Al LDH and calcined LDH catalysts, respectively, where the removal of phenol reached 77 and 83 %, respectively. However, a further increase in hydrogen peroxide (above 3mL) had a detrimental effect on phenol degradation and toxic intermediates were still observed in the
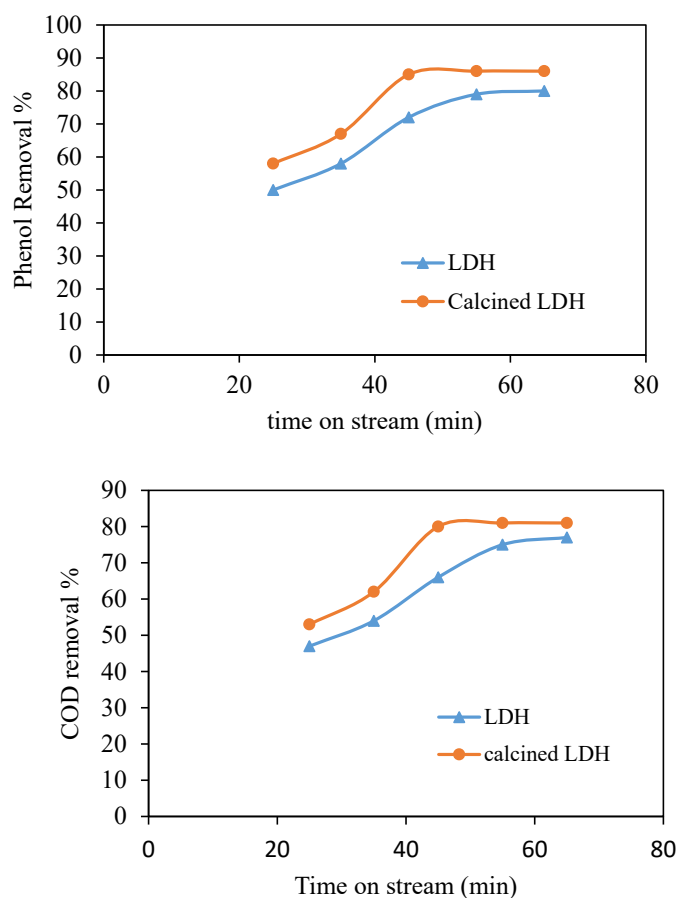
Fig.8. Phenol removal and COD removal percent at different times on stream over Mg-Al LDH and calcined LDH (reaction conditions: V = 100 mL, m = 0.05 g, initial phenol concentration: 100 mg L^{-1}, V_{H2O2}= 3 mL, temperature = 60 ºC).

reaction solution. The negative influence of excess hydrogen peroxide can be explained by the reaction (2):

$$HO^{.} + H_2O_2 \rightarrow H_2O + HO_2^{\times} \qquad (2)$$

Although another radical ($HO_2\cdot$) was produced, its standard electrode potential is lower than HO· In other words, the detrimental effect of excess hydrogen peroxide can be explained as a result of competition between hydrogen peroxide and phenol, as well as its oxidation intermediates for the hydroxyl radicals. The results are in agreement with the literature [18, 19].

Finally, the effect of reaction time on phenol removal was investigated in the CWPO process using Mg-Al LDH and calcined LDH. The results are shown in Fig.8. The maximum removal of phenol (85%) resulted at the stream on time of 45 min on calcined LDH and the phenol removal

reached the maximum value (79%) after 55 min. A similar trend was observed for COD of the solutions, just the COD removal percentage was a few percentages lower than phenol removal percentage as shown in Fig.8.

The comparison of the activity of the LDH and calcined LDH with that reported in the literature [1, 20] for the phenol removal indicated the promising activity of the present catalyst in the CWPO process. The calcined LDH, which is a mixture of LDH and mixed oxides of Mg-Al exhibited superior activity than pure LDH catalyst.

The activity of the LDH and calcined LDH catalysts was calculated based on the rate of phenol removal on the catalysts and compared with that reported in the literature. The results are presented in Table1. The concentration of the catalysts in the wastewater was 0.5 g.L^{-1}. It is observed that the rates of phenol oxidation on the calcined LDH and

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Table 1. The rate of phenol oxidation by CWPO over different catalysts

catalyst	C_0 (mmol)	Temp. (°C)	Time (min)	Conversion (%)	Rate ($mM.g_{cat} min^{-1}$)	Ref.
MgAl LDH	1.065	60	55	79	3.06×10^{-1}	This work
MgAl LDH(Calcined)	1.065	60	45	85	4.02×10^{-1}	This work
Cu-Co$_2$ oxide	1.065	50	40	81	4.3×10^{-2}	[1]
Cu-Mn$_2$ oxide	1.065	50	40	70	3.6×10^{-2}	[1]
KCl/ CuNiAlCO$_3$	2.66	40	120	94.4	4.18×10^{-2}	[21]
ZnFeO4	1.065	70	300	97	3.44×10^{-3}	[16]

LDH are much more than those reported in Table 1, indicating the superior activity of our catalysts in the CWPO process.

CONCLUSIONS

Mg-Al layered double hydroxides with carbonate interlayer were successfully synthesized and characterized. The Mg-Al mixed oxide was formed during the calcination of LDH at 500 °C. The calcined LDH was in the form of Mg-Al mixed oxide and MgO. The catalytic activity of LDH and the calcined LDH in the removal of phenol from wastewater by catalytic wet peroxide oxidation were successfully investigated. The Mg-Al mixed oxide was exhibited a considerable activity for phenol remediation which is ascribed to the synergetic behavior of MgO and Mg-Al oxide. It is concluded that the calcined LDH could be promising to be investigated in the CWPO process. CWPO process is a good alternative to the various physical and chemical methods of phenol removal because of the lack of need for difficult laboratory conditions and the absence of toxic and high toxicity production.

CONFLICT OF STATEMENT

There is no conflict of the statement in this work.

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