Synthesis of Zn-Fe layered double hydroxides (LDH) by using Zn and Fe\(^{II}\) salts and removal behavior research of anionic dye

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Abstract

With attempts to improve the synthesis of Zn-Fe-CO\(_3\) layered double hydroxides, the improved coprecipitation method by using Fe\(^{II}\) and Zn\(^{II}\) as the initial reagents at constant pH value was investigated. The obtained material was characterized by PXRD analysis, FTIR spectroscopy, and simultaneous thermogravimetric differential-scanning calorimetry (ATG/DSC). The material was obtained for molar ratios [Zn/Fe] = 1:1 to 5:1. The capacity of Zn-Fe-CO\(_3\) layered double hydroxides for removing the organic pollution (e.g., Indigo Carmine dye (IC)) was studied herein. Batch adsorption experiments were conducted to investigate the effect of various operating parameters, such as Zn/Fe molar ratios from 1:1 to 5:1, solution pH, and contact time in order to provide optimal conditions for removal. Adsorption kinetic study revealed that the adsorption process followed both first and second-order kinetics, where the percentage removal of indigo carmine a maximum value \(R(\%) = 91.52\) for a contact time \(t=90\) min, adsorbent mass 0.05g/20, concentration 0.06 g/l and initial pH of the solution. Furthermore, the influence of common inorganic anions present in the solution such as NO\(_3^-\), Cl\(^-\), CO\(_3^{2-}\) and SO\(_4^{2-}\) on the uptake of IC were also studied and an increase in the following order NO\(_3^-\) > Cl\(^-\) > CO\(_3^{2-}\) > SO\(_4^{2-}\) was observed. Zn-Fe-CO\(_3\) has a higher potential application in the indigo carmine removal field.

1. Introduction

Dyes contamination of groundwater is of major concern in various parts of the world. Dyes may cause severe damage to human beings (dysfunction of kidneys, reproductive system, liver, brain, and central nervous system) and have been characterized as carcinogenic [1], due to their toxicity, unpleasant coloring and non-biodegradation [2, 3], (Indigo carmine dye), it is difficult to be oxidized and cracked. Nowadays, many advanced types of research have been focused on treatment economic solution, adsorption techniques for dye removal from wastewaters [4, 5]
using various sorbents such as olive pomace [6] activated carbons [7], and clays [8] has been widely studied for a high-efficiency [9]. Layered double hydroxides have a considerable assuring in various fields, such as adsorption, photocatalysis, catalysis, and drug delivery or electrochemistry [10, 11]. The most important class of LDHs or hydrotalcite-like compounds can be represented by the general formula $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^x[\text{A}^{n-}\text{mH}_2\text{O}]$ where $\text{M}^{2+}$ and $\text{M}^{3+}$ are divalent ($\text{Zn}^{2+}$, $\text{Mg}^{2+}$, $\text{Fe}^{2+}$, $\text{Co}^{2+}$, $\text{Cu}^{2+}$, $\text{Ni}^{2+}$) and trivalent ($\text{Al}^{3+}$, $\text{Cr}^{3+}$, $\text{In}^{3+}$, $\text{Mn}^{3+}$, $\text{Ga}^{3+}$, $\text{Fe}^{3+}$) metal ions, respectively that occupy octahedral sites in the hydroxide layers; $\text{A}^{n-}$ is an exchangeable anion ($\text{CO}_3^{2-}$, $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{F}^-$, $\text{Cl}^-$), and $x$ is equal to the molar ratio of $\text{M}^{3+}/(\text{M}^{2+}+\text{M}^{3+})$. The layers have a brucite-like structure [12], in which the isomorphic substitution of some divalent cations by trivalent ones gives rise to the positive residual charge [13, 14] which requires the presence of interlayer anions to maintain overall charge neutrality. In this study, Zn-Fe-CO$_3$ layered double hydroxides were synthesized via a co-precipitation method at different molar ratios, we describe also the procedure for the synthesis of Zn-Fe(III) LDHs by using Fe(II). In one such process, the precipitate from Zn and Fe(II) reagents was oxidized to convert Fe(II) into Fe(III) within the solid framework. The samples were characterized by powder XRD, FTIR, and TGA/DSC. The resulting materials were then used as adsorbents for the removal of Indigo Carmine as the target pollutant, from an aqueous solution. The effects of molar ratios of Zn-Fe-CO$_3$, initial pH, equilibrium time, and the presence of inorganic anions in the solution have been studied in detail to determine the efficiency of this material under optimized conditions. The localization of the dye in the interlayer space of our sample is studied by infrared spectroscopy (FT-IR) and thermograms. In addition, kinetic models (first-order, pseudo-second-order, and intraparticle diffusion) have been also investigated.

2. Materials and methods

2.1. Indigo carmine dye

Indigo Carmine (IC), or 5,5'-indigodisulfonic acid sodium salt with the empirical formula C$_{16}$H$_8$N$_2$Na$_2$O$_8$S$_2$ and the molar mass of 466.353±0.026 g/mol, were supplied by Merck (purity > 99%). The water solubility of the dye at 25 °C is 10 g/L. The chemical structure has been illustrated in Figure 1. This dye presents a maximum absorption at $\lambda = 610$ nm.

![Figure 1](image_url). Molucular structure and UV-Vis spectrum of IC at 20 mg/L.
2.2. Synthesis of sorbents

All the steps of the synthesis were conducted using distilled water. Synthetic reagents used were at least 98-99% pure and were supplied by Biochem Chemopharma. The phases [Zn-Fe-CO₃] were obtained by the "coprecipitation" method at constant pH in the air using an aqueous solution (50 mL) containing ZnCl₂ and FeCl₂·H₂O (with a Zn/Fe molar ratio of 1:1 to 5:1 and a total metal ion concentration of 1.0 mol L⁻¹) were slowly added dropwise to 50 mL of distilled water with vigorous stirring at room temperature. During the co-precipitation reaction, the pH in the reaction mixture was maintained at a constant value of seven by the simultaneous addition of a 1.25 M NaOH solution. The suspension obtained was turquoise blue during the synthesis. The resulting suspension was aged at 313 K for 24 h. The solid products obtained were then centrifuged and washed thoroughly with deionized water and dried at 313 K for 24 h, affording a pale-yellow solid.

2.3. Materials characterization

Powder X-ray diffraction patterns (PXRD) of our samples were recorded using a Philips PW1820 diffractometer with monochromatic CuKα radiation (λ=1.5418 Å at a scan speed of 0.02 °/s) over a 2θ range of 5 to 70°. Identifications of the crystalline phases were done by comparison with the JCPDS files [15]. Powder X-ray diffraction diffractogram of Zn-Fe-CO₃ at different molar ratios are shown in (Figure 2). The XRD patterns give both sharp and symmetrical peaks with some asymmetrical peaks at a high angle, the values of their positions give the values of d₀₀₃. The d₀₀₃ crystal plane with basal spacing was observed at 7.78, 7.63, 7.68, 7.92, 7.88 Å for Zn₁Fe, Zn₂Fe, Zn₃Fe, Zn₄Fe, Zn₅Fe respectively. The purity decreases with increasing in molar ratio from 1:1 to 5:1 with the occurrence of a peak at around 16.5° in the 2:1 to 5:1 ratios that were identified as Fe₅O₇(OH).₄H₂O (JCPDS 29-0712), the intensity of this peak increases with increasing in molar ratio. However, in the PXRD diagrams, some lines cannot be ascribed to the hydrotalcite structure. The latter increase in intensity with an increase in the Zn/Fe molar ratio from 1:1 to 5:1. This is probably due to impurities or to the incomplete oxidation of iron (II) during synthesis and, from a comparison of the data with those reported in the JCPDS tables for hydrotalcite, it was possible to attribute these peaks to a simonkolleite phase (JCPDS 07-0155), or to Ferrihydrite phase (JCPDS 29-0712). Weak reflections showed a trace at: 2θ = 33.2° (Zn₁Fe); 33.30° (Zn₂Fe); 34.071° (Zn₃Fe); 33.73° (Zn₄Fe) and 32.81° (Zn₅Fe), correspond to ZnO (JCPDS file 00-001-1136). In addition, these peaks are completely absent or reduced in their intensity as the molar ratio (Zn/Fe) decreased. The values for parameter “a” are nearly constant for all samples as in Table 1. This parameter corresponds to the minimum cation-cation distance in the brucite-like layers and is related to the position of the peak due to planes (1 1 0), with a (Å) = 2d (110). The latter represents the cation-cation distance, while the value of cell constant “c” is calculated as c = 3d(003) and the values calculated are given in Table 1.

Figure 2. XRD patterns of Zn-Fe-CO₃ at different molar ratio.
Table 1. Lattice parameter at different molar ratio.

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<th>R=2</th>
<th>R=3</th>
<th>R=4</th>
<th>R=5</th>
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<td>11.58</td>
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<td>3.86</td>
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<td>3.93</td>
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<tr>
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<td>1.55</td>
<td>1.56</td>
<td>1.56</td>
<td>1.55</td>
</tr>
<tr>
<td>c (Å)</td>
<td>23.34</td>
<td>22.89</td>
<td>23.04</td>
<td>23.76</td>
<td>23.64</td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.12</td>
<td>3.10</td>
<td>3.12</td>
<td>3.12</td>
<td>3.10</td>
</tr>
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</table>

The FTIR spectra are recorded in the range of 4000-400 Cm⁻¹ by using KBr pellets technique in a Perkin Elmer FT-IR 2000 spectrometer. FTIR spectra for our samples shown in (Figure 3) are characteristic for the hydrotalcite-like structures. The broad and strong band centered at 3444.18 for Zn₁Fe LDH is common for all the hydrotalcite type materials corresponding to the asymmetric and symmetric stretching mode vibration of free OH groups and the presence of water molecules between layers [16]. The sharp absorption bands centered at 1624.16 can be attributed to the anti-symmetric stretching vibrations of carbonate anions for the Zn₁Fe LDH [17]. A series of bands in the range of 1000-400 cm⁻¹ corresponding to the existence of lattice translational modes (Zn–OH) and vibrational modes of the lattice showing the Zn-O, Fe³⁺-O, O-Zn-O or O-Fe³⁺-O bonds while the weak bands around 633.76 were assigned to unidentate carbonate symmetric stretching vibrations (O–C–O bond) for Zn₁Fe LDH [17]. The vibration bands associated with the organic anion, as well as the adsorption bands characteristic for our sample after IC adsorption are evidenced in the spectrum Zn-Fe-IC, the asymmetric stretching vibration related to the S=O bond appears between 1000 et 1125 Cm⁻¹, the band characteristic to the carbonate anion is evidenced with a considerable decrease in intensity shown in the spectrum of Zn-Fe-IC compared with spectrum ZnFe-CO₃ confirms the fact that the interlayer carbonate anions have been displaced [18].

Figure 3. FTIR spectra of: (a) Zn-Fe-CO₃ at different molar ratio, (b) Zn-Fe-IC
Thermogravimetric/Differential Scanning Calorimetry (TG/DSC) of [Zn-Fe-CO₃] and [Zn-Fe-IC] was carried out using LINSEIS.STA.PT 1600.ATG-DSC equipment, in the temperature range between 20 and 1200 °C at a heating rate of 10 °C min⁻¹ in air. The TG and DSC curves for Zn-Fe-CO₃ and Zn-Fe-IC are illustrated in (Figure 4).

The results are obtained in the form of the decay curves of the mass associated with the DSC peaks as a function of temperature where the thermogram of [Zn-Fe-IC] is different from that of [Zn-Fe-CO₃], which confirms the retention of IC. We clearly observe multiple consecutive mass losses for which the inflexion points coincide with temperatures corresponding to minima and maxima in the DSC. The first loss of mass from about 26% to 225 °C, to this loss of mass is associated two endothermic peaks at 120 °C and 225 °C correspond to loss of physically adsorbed water and water in the interfoliar space. In the range 225-600 °C, the loss of mass 3% is a combination of decarbonization and dehydroxylation of the material, this destruction takes place at the same temperature range as that for the parent material [Zn-Fe-CO₃] 525 °C. A crystallization peak appeared at 425 °C as an exothermic event due to the formation of monoxides. As well, after 600 °C we obtain oxide matrix (spinel, or monoxide), the mass loss is low when the dye is retained, coinciding with the endothermic peak in the DSC profile, it probably corresponds to the elimination of a fragment, which contains sulfur in the form of SO₂ because of its slow diffusion in the oxide matrix [19].

3. Removal study

3.1. Determination Indigo Carmine dye concentrations

The experiments were carried out in order to test the performance of removal Indigo Carmine dye by adsorption on Zn1Fe. The amount of Indigo carmine ions loading (mg) per unit mass of Zn-Fe-CO₃, Qₑ, was obtained by the following equation:

\[ Qₑ = (Cᵢ - Cₑ) \frac{V}{m} \] (1)

Where, \( Cᵢ \) and \( Cₑ \) are initial and equilibrium concentrations in mg/L, \( m \) is the mass of adsorbent in grams, and \( V \) is the volume of solution in liters. Equation (2) was used to calculate the color removal efficiency in the treatment experiment:
\[ R\% = \frac{C_i - C_e}{C_i} \times 100 \] (2)

The concentrations of IC in the supernatant are determined eventually from standard curve obtained using UV-Vis spectrophotometer (Spectrum instruments SP-UV 200S) by measuring the absorbance at 610 nm.

Due to the inherent bias resulting from the linearization of the isotherm models, the non-linear regression Root Mean Square Error (RMSE), the Chi-Squares (\( \chi^2 \)), and normalized standard deviation (\( \Delta q \)) test methods are employed as criteria for the quality of fitting using Equations (3), (4), and (5), respectively.

\[
RMSE = \sqrt{\frac{\sum_{i=1}^{n} (q_{e,exp} - q_{e,cal})^2}{n}}
\] (3)

\[
\chi^2 = \sum_{i=1}^{n} \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}}
\] (4)

\[
\Delta q = \sqrt{\frac{\sum_{i=1}^{n} \left( \frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right)^2}{n-1}}
\] (5)

Where, \( q_{e,exp} \) and \( q_{e,cal} \) are, respectively, the experimental and calculated adsorption capacities as calculated from the model (mg.g\(^{-1}\)), and \( n \) is the number of experimental data points. Smaller values correspond to better curve fitting.

3.2. Effect of molar ratios of Zn-Fe-LDH, on dye removal

The effect of the molar ratios of synthetized sample on IC adsorption was examined by mixing 0.05 g/L of IC by with 0.05 g of each LDH for 24 h agitation time in total volume of 20 ml. Figure 5 show a decrease on removal efficiency gradually as the molar ratio increase; furthermore, the first molar ratio show high capacity of 98.04% for removal of IC, as confirmed by PXRD this behavior can be attributed to the high purity of ZIF-LDH instead other molar ratios.

![Figure 5. Effect of molar ratios of Zn-Fe-CO\(_3\) on removal of IC dye.](image-url)
3.3. Initial pH effect on dye removal

The pH of the solutions has a large ionic contribution that can influence the adsorption process. The removal of IC dye at different pH values ranging from 3 to 12 by Zn1Fe was studied, the suspension pH was prepared by adding 0.05 g of LDH to 50 ml of dyes solutions (60 mg/L) for 48 h, the initial pH values of solutions were adjusted by adding 0.01 M HCl or 0.01 M NaOH. The final pH was measured at the end of the experiments. Figure 6 shows the variation of the removal efficiency of IC at different pH values. As can be seen, the adsorption of IC is obviously dependent on the initial solution pH. Maximum adsorption of dyes increased in acidic pH from 3.0 to 5.5 and decreased as the solution pH is above 5.5.

![Figure 6. Effect of pH on the adsorption of IC by Zn1Fe-LDH.](image)

The results (Figure 7) indicated that pH of zero point charge (pH\(_{\text{pzc}}\)) of Zn-Fe-CO\(_3\) is around 6.1. Let’s recall that the surface of LDH consists of hydroxyl groups (▬OH); thus, when pH increases above pH\(_{\text{pzc}}\), the hydroxyl groups are ionized and the negative charge density on the surface increases. While at lower pH values below pH\(_{\text{pzc}}\), the surface of LDH becomes protonated and gets more positively charged, the electrostatic attraction occurs between the positively charged active adsorption sites and the anionic dye molecules, which results in an increase of dye removal. This why the maximum adsorption occurred at pH 5.5, similar phenomena are previously reported for Mg-Al-LDH [20]. Following these experiments, it was decided to carry out the retention experiments at the natural pH of the solution (LDH+ dye solution) (pH= 5.8).

![Figure 7. pH\(_{\text{pzc}}\) of Zn1Fe-LDH.](image)
3.4. Adsorption kinetics

The effect of sorption time on IC removal with Z1F-LDH is shown in (Figure 8), a period ranging from 5 to 120 min with ratio solid/solution of 1 g/L at initial pH 5.8 and initial dye concentration of 50 mg/L.

The figure indicates that the quantity of dye adsorbed increased within the first 60 min and then continue to increase at a relatively slow speed until a state of equilibrium is reached within 90 min. Hamouda et al [8] reported similar phenomena in their study of the adsorption behavior trypan blue on hydrotalcite, the optimal time of 90 min was the sufficient time for stabilization of this adsorbent and adsorbate dispersed solution. According to several authors [21, 22], the adsorption can be controlled by the transferring step of the adsorbate through the outer liquid film and/or of the diffusion of the solute within the adsorbent particle. Kinetic modeling not only allows estimation of sorption rates but also leads to suitable rate expressions characteristic of possible reactions mechanisms.

\[
\frac{1}{Q_t} = \left( \frac{k_1}{Q_e} \right) \left( \frac{1}{t} \right) + \frac{1}{Q_e} \\
\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \\
Q_t = k_i t^{0.5} + C
\]

where \( Q_t \) is the amount of Indigo Carmine sorbed (mg/g) at a given time \( t \), \( Q_e \) is the maximum adsorption capacity (mg/g), \( k_1, k_2 \) and \( k_i \) are the pseudo-first-order, pseudo-second-order, and intra-particle diffusion rate constants, in (min\(^{-1}\)), (g.mg\(^{-1}\).min\(^{-1}\)) and (mg g\(^{-1}\).min\(^{0.5}\)) respectively, \( t \) is the agitation time in (min) and \( C \) (mg g\(^{-1}\)) is the intercept.

As shown in (Figure 9b) and (Table 1), the high correlation coefficients for the pseudo-second-order model (0.99), as were the law values of \( \Delta q, \chi^2 \) and RMSE for first order models suggested that the adsorption process followed both pseudo-first and second-order kinetic model, the good fit with experimental data confirm that the velocity control mechanism of adsorption is

![Figure 8. Effect of contact time on adsorption of IC on Zn1Fe-LDH (C0= 60mg/L, m/V=1, T=25 °C).](image-url)
chemical adsorption.
In order to verify if the intra-particular diffusion model is adapted to our experimental data, we have plotted Qt vs. t^{0.5} (Figure 9 c). The value of the scattering constant k is given in Table 1. Figure 9c shows that the adsorption of IC on Zn1Fe-LDH follows this pattern up to 90 min.

**Figure 9.** Kinetic plots for adsorption of IC on Z1F-LDH: a) pseudo-first-order plot, b) pseudo-second-order plot, and c) intraparticle plot.

The calculated kinetic parameters for Indigo Carmine sorption by Zn1Fe-LDH are given in Table 2.
Table 2. Adsorption kinetic parameters of IC dye on Zn1Fe-LDH.

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3.5. Effect of the competing anions

The effect of the presence of inorganic anions (NO$_3^-$, Cl$^-$, CO$_3^{2-}$ and SO$_4^{2-}$) on IC adsorption was examined by mixing variable anion/dye concentration ratios (1/2, 1/1 and 2/1) along with 60 mg/L of IC by fixing the dose of LDH at 0.05 mg for 90 min agitation time in the total volume of 50 ml (Figure 10) showed that both the type and the concentration of the anions affected the adsorption with a decrease on adsorption of IC gradually as the concentrations of competitive anions increase; furthermore, the presence of carbonate and sulfate anions influenced strongly on the removal ability of IC molecules, instead of chloride and nitrate in the following order: SO$_4^{2-} >$ CO$_3^{2-} >$ Cl$^- >$ NO$_3^-$. This confirms the proposition of Miyata [26] which assumes that the LDH materials have more affinity toward anions with higher charge density.
Figure 10. Influence of several inorganic anions on the IC adsorption by Zn1Fe-LDH.

4. Conclusion

In conclusion, we have shown that zinc-iron(III) layered double hydroxides (LDHs) with different ratios can be prepared from zinc and iron(II) precursors even with a molar ratio of 1:1 it is possible. It can be seen that Zn-Fe-CO$_3$ LDH (molar ratio Zn:Fe = 1:1) synthesized at pH=7 has been found with good purity and crystallinity instead other molar ratios. The purity of prepared Zn-Fe-CO$_3$ decrease with increasing in molar ratios of Zn:Fe from 1:1 to 5:1. The results show that the sorption of Indigo Carmine dye on our sample can remove a considerable amount of this dye from aqueous solutions, natural pH of the solution (dye +LDH) gives rise to high adsorption capacity. FTIR analysis after adsorption of IC showed the presence of the vibration bands associated with the organic anion in the interlayer region, indicating that the IC could be adsorbed on our samples. TG/DSC analysis of Zn-Fe-CO$_3$ after adsorption indicates that the LDH stabilizes IC and delays the combustion of adsorbed molecules. The presence of competing anions influenced strongly on the removal ability of IC molecules, a decrease in the following order: SO$_4^{2-}$ > CO$_3^{2-}$ > Cl$^-$ > NO$_3^-.$

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References