Effect of pH on the adsorption behaviour of Congo Red Dye on the Mg-Al layered double hydroxide

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Abstract. In the present study, the synthesis of Mg-Al layered double hydroxide at the molar ratio of 3:1 for Mg/Al are determined. One-step hydrothermal technique with slow hydrolysis of urea at a low temperature was employed without further annealing. The study was aimed at determining the effectiveness of Congo Red dye removal in the adsorption process onto Mg-Al layered double hydroxide (LDH) with respect to the change in pH of the solution. The experiment was conducted at concentrations of a sorbent 0.04g with 100 ml of Congo Red and at six values of the reaction, i.e. pH 2.0, pH 4.0, pH 6.0, pH 8.0, pH 10, and pH 12.0. It was found that pH affects the adsorbent surface charge and the degree of anionic dye dissociation. This can be explained to the chemical form of dye in the solution and functional groups present on the adsorbent surface at a specific pH.

Keywords: Congo Red Dye, Mg-Al layered

1. Introduction

Industrial development is one of the key drives for developing countries including Vietnam. Parallel to the benefits it brings, the problem of environmental pollution is increasingly serious, i.e. water pollution which is caused by the waste water from the garment industry. Dye effluent has been one of the largest contributors to the worsening ecosystem and consequently, deteriorating human health in deprived areas [1–4]. Removal of dye in the aqueous solution is difficult due to its chemical inertness and complex aromatic structures, conferring the substances resistance against sunlight, water, soap, and oxidizing agents. In the previous studies, the removal of various types of dyes have been attempted via physical, chemical and biological treatment methods. Although these efforts achieved some successes, they have several disadvantages including high operation and investment costs, and secondary sludge disposal problems [5–7].

The process of adsorption enables to remove not only colour-producing compounds but also other substances posing threat to the natural environment [8–14]. Processes of dyes removal from wastewaters...
require substantial financial outlays. In contrast to chemical and physical processes, i.e. chemical and electrochemical oxidation, coagulation, membranous processes, flocculation or ion exchange, the process of adsorption does not require relatively high financial expenditures [8-14]. With appropriate adsorbents - characterized by its availability and the feasibility of regeneration - may assure high effectiveness of contaminant removal.

Among the numerous types of sorbents, nanocomposites have attracted widespread attention [15–17] and layered double hydroxides (LDH) has gained special attention in fabrication of new materials that could be used in various science and technological applications. LDHs are classified as ion lamellar crystal that is made up of three main components: positively charged brucite-like host layers, and the interlayer anions between host layers to balance charge and solvent molecules [18–20]. The appeal of the material lies in its positively charged layers, large interlayer spaces and the abundance of exchangeable anions, making LDHs suitable for applications involving treatment of water contaminated with anionic and cation dyes. Structurally, the stacked layers of LDHs were formed by a positive layer (M\(^{2+}\),M\(^{3+}\)-(OH)\(_{2}\)\(^{+}\)) and exchangeable anions (A\(^{x-}\),x), creating 2D layered nanosheets. The unique structure confers LDHs multiple useful characteristics. Among them, the ability of the metal cations of the adsorbent to be tunable in the host layers figures.

In this work, The simple method to synthesize Mg/Al LDHs by hydrothermal reaction at the different temperatures are determined. We conducted experiments to study the adsorption of LDHs by removing Congo Red from aqueous solutions. The scope of the research included determination of the effect of pH value on the effectiveness of Congo Red Dye adsorption onto the Mg-Al LDH.

2. Materials and Methods

2.1. Preparation of Mg-Al LDHs adsorbent

MgCl\(_2\).6H\(_2\)O (98%), AlCl\(_3\).6H\(_2\)O (97%) and urea (99%), purchased from Sigma Aldrich. A mixture containing AlCl\(_3\).6H\(_2\)O (8 mmol), MgCl\(_2\).6H\(_2\)O (4 mmol), urea (128 mmol), and 60 mL of distilled water was magnetically stirred for at 3000 rpm for 15 min in beaker. The resulted mixture was introduced into a 100 mL Teflon - lined autoclave, which was then subjected to heating at 100°C, 150°C, 180°C for 24 h in an oven with stirring. Finally, centrifugation took place at 5000 rpm for 10 min to obtain the white powder precipitate, which was then washed with deionized water and ethanol several times, dried at 110 °C for 12 h and stored in dessicator for further use.

2.2. Preparation of congo red (CR) solution

Industry-grade Congo Red dye was used in this study. The dye stock solution 1000 mg/l was prepared in deionized water derived from consecutive dilutions. CR concentration in the experiment was determined following a linear calibration curve which built from 0 to 20 mg/L, established by measuring absorbance of CR solutions at different concentrations via a DR5000 spectrophotometer (HACH, USA) at \(\lambda_{\text{max}}\) of 570 nm.

2.3. Adsorption experiments

The adsorption capacity of the as-synthesized LDHs was analyzed by conducting batch adsorption experiments using congo red dye. The effect of temperature synthesis (100 °C, 150 °C và 180 °C), contact time (5 – 210 min), and initial congo red concentration 20 mg/L at 200 rpm on the adsorption of congo red. Typically, each test was conducted in a 150 mL beaker containing 100 mL of the dye solution and 0.04 g of Mg-Al LDHs. At a time interval, about five mL of solution was withdrawn using a plastic cylinder, and the solid was removed by centrifugation at 9000 rpm to obtain a clear solution. The concentration of residual dye was then analyzed by UV-Vis spectrophotometer analysis. The following equation estimated the equilibrium adsorption capacity of adsorption: 

\[
q_e = \frac{(C_0-C_e)}{m} V, \quad \text{Eq (1)}
\]

where \(C\) (mg/L) are concentrations of dye solutions, \(q\) (mg/g) is the adsorption amount, \(m\) (g) is the mass of Ca-Al LDHs and \(V\) (L) is the volume of the solution. The subscript 0 and e denotes initial and equilibrium, respectively. Triplicate measurements conducted to obtain average numbers.
2.4. Effect of pH solutions

The pH of CR solutions was adjusted from 2 to 12 using 0.1N HCl or 0.1N NaOH solutions to investigate influence of pH on CR removals. The initial CR concentration was kept at 40 mg/L. After the adsorption lasted 30 min, the solution was centrifuged at 3000 rpm for 30 min to separate the supernatant. Quantification of CR in solutions was performed using a DR5000 spectrophotometer (HACH, USA) at 570 nm.

3. Results and discussion

3.1. Characterization of Mg/Al LDHs:

The chemical nature of the original Mg containing elements alters the process of creation of the synthesis products. It is clear present in the results of X-ray diffraction (Fig. 1a).

![Figure 1](image)

**Figure 1.** (a) X-ray diffraction and (b) SEM of Mg/Al LDH at different temperature: at 100 °C, 150 °C and 180 °C, respectively.

In the previous, most of the previous view regarding the effect of temperature synthesis was reported [21,22]. The temperature of synthesis process is one of the important factors impact to shape and structure of materials. To study the structure modification of hydrotalcite phase on heating, the sample was carried out in the temperature range of 100 – 180 °C. Clearly, the Mg / Al LDH specimens with distinct crystalline and shape form were acquired at distinct temperature synthesis. In addition, the patterns shows in Fig.1a also reveal that the sharp and strong intensities achieved at 100 °C. All patterns reveal peak close to 20 = 11 °, 23 °, 34 °, and 60 ° corresponding to the (003), (006), (012), (110) and (1013). The basal spacing of d003, d006 decreased with an increase temperature and disappeared at 180 °C due to dehydration of interlayer water molecules and dehydroxylation. Aside from, the presence of cubic MgO was observed d220 at 62.6°. 20. Furthermore, SEM analysis data shows the same crystal morphology as in the samples with aluminum hydroxide, comprised of many standardized, three-dimensional, flower-like constructions (Fig. 1b). The increasing temperature of the hydrothermal process causes the decrease in crystallite sizes, and appears more defects onto the surface. It can be clarified that when temperature rises,dehydroxylation along with decarbonation occurred, which results in the destruction of the layered structure of hydrothalcite, and mixed oxide formation has been noted. The result is in agreement with the previous studies [23]. Besides, it is well recognized that crystals of uniform crystalline size show greater adsorption effectiveness.
The thermal properties of Mg/Al samples were investigated by thermogravimetric analysis (TGA) which presented in Fig.2. By differentiating the TGA curves, more thorough data on the subtlety of heat behavior can be acquired as shown in the DTG curves. Specifically, LDHs have two distinct events around 200 °C and 400 °C. At below 200 °C, the loss weight was found due to the desorption of physisorbed and intercalated solvents. At the next stage, the hydroxyl groups begin decompose and gradually form the LDH structure. It is normally ascribed to the complete dehydroxylation of the metal hydroxide layers, reaches at around 400 °C. Interestingly, when temperature of synthesis process is 180 °C shows the weight loss and derivative weight curves rapid, one-step degradation. The inflection temperature and end temperature of Mg/Al LDH also observed are 550–700, which illustrate that this structure can be assigned Al₂O₃ [24]. This is a important distinction and is primarily due to better dispersion of Mg/Al LDH particles at the different temperature.

3.2. The effect of pH solution to adsorption capacity

First, the salt addition method was employed to determine the point of zero charge (pHₚZC). To be specific, 0.1 M KCl solution was prepared and had its initial pH adjusted to vary from 2.0 and 12.0 using HCl and NaOH solution. Following that, a 250 mL beaker containing 100 mL of 0.1 M KCl and 0.04 g of Mg-Al LDHs was prepared and allowed to stabilize for 24h. The final pH was measured by multi-parameter analysis [17]. The pHₚZC was calculated from this Figure 3 at the point where pH = 0. From figure 3, it could be observed that at different temperatures the pHₚZC value varies. Specifically, at 100 °C, 150 °C and 180 °C, pHₚZC is 7.3, 6.8 and 6.98, respectively. The temperature is known the one of factors direct effect to the pHₚZC values of material [25]. In particularly, at 100 °C, pHₚZC is highest, between at 150 °C and 180 °C the PZC values were similar. The PZC differences in thermal treatment samples showed a close relationship with the subsequent chemical transformations of Mg/Al LDH. According to the results analysis above, it would be be possible to infer that magnesium oxide and aluminium oxide partially covers the material surface which make the difference of pHₚZC values.

Changes of dye adsorption by Mg-Al LDHs could be described relative to the point of zero charge (PZC), where the net total particle charge is zero. Figure 1 indicates that the PZC of Mg-Al LDHs at 100°C was 7.3, agreeing with a previously reported value [26]. Apart from positive charge caused by isomorphic substitution, it is suggested that variables charges might existed due to the adsorption of ions H⁺ or OH⁻ to Mg-Al LDHs [27]. On the other hand, at pH lower/higher than the PZC, the protonation/deprotonation of the hydrated surface of the Mg-Al LDHs took place, subsequently imposed positive/negative charge of the adsorbent surface. The mechanism by which OH⁻ are consumed is twofold, described by a previous study [23]. First, commensurate with our previous explanation, ion adsorption could be due to the binding of surface hydroxyls to metal ions on the surface. Second, the adsorption could be caused by anionic exchange of nitrate anions in the interlayer by hydroxyl anions of the solution.
By varying pH value of the solution from 2 to 12, the influence of pH on CR dye removal efficiency could be investigated. Prior to the adsorption experiment, the desired pH was achieved by adding dropwise of NaOH or HCl to the solution while maintaining the initial dye concentration and adsorbent dosage at 20 ppm and 0.04 g, respectively. Figure 4 graphs the adsorption efficiencies of the Mg-Al LDH at various pH values. It was showed that pH parameter has significantly affected to the adsorption of CR with the adsorbent surface. The phenomena could be explained by the nature of CR dye, which is sensitive to pH and the transition of azo group to higher wavelength, caused by protonation when adding HCl. In highly acidic solution, the cationicity of the dye prevails and two forms of CR, namely ammonium rich and azonium variety, emerge due to protonation. While the former is abundant in fresh solution, the latter presents markedly in the solution after 1 h, at which point the isoelectric point of CR approximates 3. Peak adsorption of CR were found at pH 6 in the first two investigations with the temperature of 100 °C and 150 °C whereas pH 4 is the value in which peak adsorption was achieved in the third investigation at 180 °C. This can be explained based on pKa value of CR (pKa = 4.1) and pH\(_{PZC}\) of LDHs. To the best of our knowledge, between the particles and the local electrical field that cover around the nucleus have an interaction which mentioned in DLVO theory. Corporeality, it describe the appealing forces of London– van der Waals (V A) and the electrostatic repulsion (V R) between two charged electrons owing to electrical double layer overlapping. Since hydrogen ions abundantly present in the solution with lower pH, the surface of the adsorbent becomes positively charged and in turn electrostatically attracts the negatively charged dye molecules. On the other hand, at the higher solution pH, the adsorption ratio was found to be declining. Notably, the difference in the equilibrium of adsorption can be related to their physicochemical properties and structure [28]. Therefore, the pH of the solution should be maintained at the value of marginally higher than 4 to achieve the highest CR. Ideally, CR adsorption should take place in the weak acid or neutral condition.

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**Table 1.** pH\(_{\text{init}}\) and pH\(_{\text{after}}\) of solution before hydrotherm.

| Sample   | pH\(_{\text{init}}\) | pH\(_{\text{after}}\) |
|----------|----------------------|----------------------|
| M100 °C  | 3.09                 | 8.4                  |
| M150 °C  | 3.09                 | 9.0                  |
| M180 °C  | 3.09                 | 9.26                 |

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Figure 4. Effect of pH solutions on the CR adsorption onto Mg/Al LDHs (a) M100°C, (b) M150°C, (c) M180°C

4. Conclusions
Mg-Al layered double hydroxide was successfully synthesized and investigated for removal capabilities against Congo red dye with regard to pH changes in the aqueous solution. By varying the pH from 2 to 12, it was implied that pH drastically alters the surface charge of Mg-Al LDH, subsequently the removal of dye. It is also suggested that solutions of very low pH may cause the dye molecules to dissolve which not suitable for adsorption and that the pH of 6 is optimal for achieving best dye adsorption.

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