Application of Magnetite Zn/Al Layered Double Hydroxide (Fe$_3$O$_4$ Zn/Al LDH) on the Removal of Organic Matter in Supplying Water

Nguyen Thi Thanh Phuong, Tran Thi Minh Ha, Tran Ngoc Han, Sri Juari Santosa

Abstract—In this study, magnetite Zn/Al layered double hydroxide (LDH) composite has been synthesized through the chemical co–precipitation method. Raw water samples of Thu Duc and Tan Hiep water plant were also collected and analysed, they were used as the object to investigate dissolved organic compounds (DOC) adsorption capacity of the material. The results of DOC empirical adsorption experiments in raw water samples of Thu Duc and Tan Hiep water plants also show that the adsorption processes reach high efficiencies when the sample solutions are adjusted to pH from 5 to 6. After 21 hours, the adsorbent in column loses its adsorption ability with the corresponding adsorption capacity of 8.12 mg/g.

Index Terms—adsorption, magnetite Zn/Al layered double hydroxide, organic matter removal, supplying water.

INTRODUCTION

Natural organic matters (NOMs) is a complex mixture derived from the decomposition of plants and animal carcasses. This mixture includes humic substances (humic acid, fulvic acid) and non-humic substances (protein, carbohydrate), while most of humic substances are identified to be precursors of disinfection by-products (DBPs) when they react with chlorine during the water disinfection process. DBPs are proved to cause birth defects, genotoxic effects and even cancer to animals and human races [1]. In addition, high NOMs amounts in water sources also have negative effects on supply water treatment processes. For instance, high amount of NOMs not only reacts with chlorine to form toxic DBPs (THMs, HAAs, HANs) and lower disinfection capacity, but also requires more treatment chemicals and materials in order to meet effective results [2]. Facing such challenges, various technologies, such as adsorption, coagulation, electrochemical coagulation, membrane filtration and advanced oxidation processes [3], are focused for the removal of NOMs. Out of all the measurements, adsorption is considered one of the most cost-effective and easy-handling methods for pollutants removal in water [4]. Adsorption is the process in which atoms, ions or molecules from a gaseous, liquid, dissolved solid substance adhere to the surface of an adsorbent. Common adsorbents comprise of aluminium oxide, iron oxides, silica gel, zeolites, activated carbon or phenol formaldehyde resin [5]. Nowadays, synthetic and hybrid materials are encouraged to be widely researched and applied in water treatment due to its high adsorption capacity, less toxicity and high regeneration ability.

The magnetite-based adsorbent with Zn – Al layered double hydroxide (Magnetite Zn – Al LDH) is a new material. LDH, or hydrotalcite, is a
group of nanostructured anionic clay materials, which has an adjustable large and porous surface. It can be found in nature or easily synthesized using co-precipitation between Zn(NO$_3$)$_2$ and Al(NO$_3$)$_3$ in alkaline solution [6]. After synthesis, Zn – Al LDH is then combined with magnetite Fe$_3$O$_4$ to create magnetic properties and, thus, enhance its adsorption effect, since pollutant particles are attracted and adsorbed to the surface of the magnetite particle in the presence of the magnetic field through the amphoteric hydroxyl group [7]. Adsorption possibility when using LDH and magnetite LDH to remove organic matters is studied by S.J. Santosa et al. (2007) [6], S.J. Santosa et al. (2008) [8], S. Mandal et al. (2012) [9], Sulistyaningsih et al. (2013) [10] and M. Lim and R. Amal (2014) [11].

Being in a tropical and a temperate zone, the amount organic compounds in the water bodies in Vietnam is awfully high, which leads to serious problems as inadequate removal of organic matters in domestic water use could cause severe damage to public health. However, such cost-effective and state-of-the-art adsorbent has not yet received proper attention from the authorities and stakeholders. As mentioned, in Vietnam, few application of magnetite-based materials or mix of these materials for water treatment [12, 13]. Approaching the trend of using natural, inexpensive and non-toxic mineral materials, this study hybridized the magnetite Zn – Al LDH adsorbent, investigated the presence of NOMs in raw water sources and evaluated the adsorption efficiency of organic matter by the above material.

2 MATERIALS AND METHODS

2.1 Hybrid of magnetite Zn/Al layered double hydroxide (Fe$_3$O$_4$ Zn/Al LDH)

**Synthesis of Fe$_3$O$_4$**

2.78 g of FeSO$_4$.7H$_2$O and 2.705 g of FeCl$_3$.6H$_2$O were dissolved in 25 mL of distilled water. A NH$_4$OH 3.5 M solution was added dropwise into the Fe$^{2+}$/Fe$^{3+}$ solution while stirring at with N$_2$ aeration until its pH reached 11. By then, a black precipitate immediately appeared. The solution was kept being stirred for the next 90 minutes at 50°C and then let cool down. The precipitate was filtered out from the mixture using 0.45 µm filter paper, washed by distilled water and dried at 60 – 70°C. Finishing product of Fe$_3$O$_4$ was then crushed and sieved by Fisher at less than 200 meshes.

**Synthesis of Fe$_3$O$_4$ – Zn – Al LDH**

Based on the study of S.J. Santosa et al. (2007), 5.949 g Zn(NO$_3$)$_2$.6H$_2$O and 3.751 g Al(NO$_3$)$_3$.9H$_2$O were dissolved in 50 mL CO$_2$-free distilled water to make a solution with Zn$^{2+}$:Al$^{3+}$ = 2:1 [6]. NaOH 0.5 M and the solution of Zn$^{2+}$:Al$^{3+}$ was added to a mixture of 0.325 g Fe$_3$O$_4$, which had been dispersed in 25 mL CO$_2$-free distilled water, while stirring until the solution pH reached 7. After 15 hours of stabilizing, the product was pyrolyzed at 120°C for 5 hours. Formed dark precipitate was...
cooled to room temperature, filtered using 0.45 µm filter paper, washed and dried at 80 °C. The final precipitate of Fe$_3$O$_4$ – Zn – Al LDH was then crushed and sieved by Fischer at less than 0.074 mm.

**Fig.1** shows the difference between Fe$_3$O$_4$, double layered hydroxide (LDH) and magnetite Zn – Al LDH. Fe$_3$O$_4$ and magnetite Zn – Al LDH are magnetic so they are attracted by magnets. Besides, the color of magnetite Zn – Al LDH is brown while those of Fe$_3$O$_4$ and Zn – Al LDH are black and white, respectively, distinguishing the three adsorption materials.

**Fig.2** demonstrates SEM images of magnetite Zn – Al LDH at 3,000×, 5,000× and 10,000× magnitude, suggesting that the surface of the material is not homogenous. At a magnification of 10,000×, multilayered structure of the material is clearly illustrated. Hollow blocks of different sizes, thereby creating the microfuge of the material. The results of experiments to determine the point of zero charge (pH$_{PZC}$) of magnetite Zn/Al LDH show that the difference in pH value is significant (ΔpH = -0.02), so the study selected pH value of 5 is the non-zero charge of the material.

2.2 Removal of dissolved organic compounds in supplying water

**Raw water sources**
Raw water samples were taken from the inlets of Tan Hiep water plant, Tan Hiep Commune, Hoc Mon District, and Thu Duc water plant, Thu Duc District, in Ho Chi Minh City. Samples were stored in plastic containers, labelled with time and place of sampling. Samples after collection are cold preserved and analyzed. The sampling and processing process was carried out in accordance with ISO 5667-3:2003. The characteristics of the untreated water samples are shown in **Table 1**.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Tan Hiep Water Plant</th>
<th>Thu Duc Water Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.21</td>
<td>7.73</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>4.97</td>
<td>8.03</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>4.48</td>
<td>6.18</td>
</tr>
<tr>
<td>UV$_{254}$ (mg/L)</td>
<td>0.097</td>
<td>0.130</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>38</td>
<td>47</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>28</td>
<td>33</td>
</tr>
<tr>
<td>Cl$^-$ (mg/L)</td>
<td>23.6</td>
<td>21.3</td>
</tr>
<tr>
<td>NH$_4^+$ (mg/L)</td>
<td>0.15</td>
<td>0.20</td>
</tr>
</tbody>
</table>

**Organic matter adsorption by static method**

**Experiment 1: Effect of initial pH**
pH of raw water samples from each water plant was adjusted to 2, 3, 4, 5, 6, 8, 10 and 12 using NaOH 0.1M and HCl 0.1M solutions. 20 mg of magnetite Zn – Al LDH were weighed and added to 20 mL of each prepared samples. The mixtures were then stirred continuously for 5 hours, filtered through Whatman 42 filter paper and measured its absorbance at 254 nm (UV$_{254}$), following by the analyses of dissolved organic carbon (DOC) in the filtered solutions for treatment comparison.

**Experiment 2: Effect of the amount of adsorbent**
pH of raw water samples from Thu Duc water plant was then adjusted to the optimal pH value identified in the first experiment using the same two chemicals. Different quantities of magnetite Zn – Al LDH which were 5, 10, 20, 30, 40, 50, 75, 100, 125, 150, 200, 250, 300, 350 and 400 mg were used per 150 mL of each sample in order to investigate alteration in the treatment efficiency due to changes in the amount of adsorbent. The subsequent treatment procedure was the same of the previous experiment.

**Organic matter adsorption by continuous flow method**

The experimental setup is illustrated in **Fig.3**. Water samples from Thu Duc water plant, pH of which were adjusted to the optimal value in experiment 1, were stored in the water container. They were then pumped downward into the adsorption column containing water – saturated magnetite Zn – Al LDH material with the speed flow of 2 mL/min, corresponding with 24.46 cm/h and a total flow of 9.8 mL/min. The height and diameter of the column were 22 and 2.5 cm, respectively, while the height of the adsorbent placed inside the column is 2.5 cm, which weighed 4.75 g. Effluent from the adsorption column was collected every 30 minutes and measured for its absorbance at 254 nm (UV$_{254}$). Thence, the
amounts of DOC adsorbed by the studied material and those remaining in the water samples were calculated for further evaluation. The experiment was carried out with static and continuous flow method to identify in the column, adsorption efficiency, optimal contact time and maximum time limit for magnetite Zn – Al LDH to be fully adsorbed.

**Analysis**

Since many organic molecules are structurally diverse in nature, the amount of NOMs in water bodies is usually measured by analyzing dissolved organic compounds (DOC) or total organic carbon (TOC). DOC and TOC were analyzed using the Analytik Jena TOC analyzers (Multi N/C 2100 model) at the Institute for Environment and Resources, VNU – HCMC. The process of determining and calculating TOC and DOC content in water samples shall be in accordance with ISO 8245:1999. According to Edzwald and Tobiason (2011), DOC analysis could be performed by measuring the absorbance of the solution at 254 nm (UV$_{254}$). UV$_{254}$ of the studied samples are measured using UV-VIS SPECORD 40 of Analytik Jena at the Department of Environmental Engineering, Tay Nguyen University. This spectrophotometer supports the spectrum from UV to NIR (190 – 1100 nm). All chemicals used in this study were analytical grade from Merck (Germany).

3 RESULTS AND DISCUSSION

3.1 Effect of initial pH

![Graph](https://via.placeholder.com/150)

**Fig 4. Effect of pH on UV$_{254}$**

**Fig 5. Effect of pH on the DOC adsorption efficiency on Thu Duc water samples**

According to **Fig.5**, the magnetite Zn – Al LDH’s adsorption effect on DOC at low pH medium (2 to 6) suggests higher performance (DOC removal of 70.74% at pH 6) than at high pH medium (7 to 12). DOC concentrations measured in the samples are relatively low, which are 4.48 mg/l for Tan Hiep water plant and 6.18 mg/l for Thu Duc water plant. Because of the small DOC amount, the humic acid content in these samples could not be quantified. Instead, this leads to the prediction that the DOC content of samples mainly consists of non – humic substances, organic micronutrients and organic matter from waste sources. Thus, the adsorption mechanism in this case could be explained by the electrostatic attraction between the adsorbent and charged organic components in the near neutral pH medium (pH of 5 to 6). Under the influence of the magnetic field generated by the Fe$_3$O$_4$ component of the material and the electric field caused by the dipole of the organic molecules, the adsorbent is induced dipole by electromagnetic force, then the adsorbents and adsorbates will attract each other by repulsion forces. Same phenomenon has been reported by El-Magied (2016) with the application of Fe$_3$O$_4$ on the removal of uranium (VI) [14].

3.2 Effect of the amount of adsorbent

Since the DOC concentrations in raw samples of Tan Hiep water plant and Thu Duc water plant are not remarkably high and there is no significant changes in DOC concentration between sampling periods, the determination of adsorption capacity of magnetite Zn – Al LDH ($q_e$, mg/g) is achieved by fixing the concentration DOC of the initial sample ($C_o$, mg/L) while changing the amount of...
adsorbent used (m, mg) based on the equation as follows:

$$q_e = \frac{V \times (C_0 - C_e)}{m}$$  \hspace{1cm} (1)$$

With $V$ is the water sample volume (L) and $C_e$ is the remaining DOC content after treatment (mg/L). The static adsorption model is established for 5 hours to reach equilibrium.

The results shown in Fig.6 show that the value of UV$_{254}$ reduces rapidly when the amount of magnetite Zn – Al LDH material increases from 5 mg to 150 mg, meaning that the adsorption efficiency increases. For the samples which are treated with more than 150 mg adsorbent, the adsorption effect does improve but not significantly. Meanwhile, according to the linear equation of below isothermal graph, the correlation coefficient is determined as $R^2 = 0.9047$ and the maximum adsorption capacity ($q_{max}$) of magnetite Zn – Al LDH is 22.47 mg/g. On the other hand, Xing et al. (2008) also used granular activated carbon (GAC) to treat DOC in synthetic biologically treated sewage effluent (BTSE), synthetic primary treated sewage effluent (PTSE), real BTSE and real PTSE. Results show that $q_{max}$ of the models are 13.88 mg/g, 9.82 mg/g, 45.80 mg/g and 10.12 mg/g, respectively, at different doses of GAC [15].

### 3.3 Surface morphology of magnetite Zn – Al LDH after adsorption

SEM images of magnetite Zn – Al LDH sample’s surface morphology before and after adsorption are demonstrated in Fig.7. SEM images at three different magnitudes of 3,000, 5,000 and 10,000 times exhibit distinct differences before and after DOC adsorption. The surface and capillaries of the post-adsorption material are covered by the adsorbed components, making the material’s surface more homogeneous than the original. Meanwhile, the material samples after adsorption have the gaps almost filled up. This phenomenon is the most evident through 10,000x magnitude SEM image. The comparison of the surface morphology of the pre- and post-adsorption materials is a testimony of the adsorption capacity of the hybrid of magnetite Zn – Al LDH.
Organic matter adsorption by continuous flow method

Fig. 8 shows the DOC adsorption curve over time by continuous flow method. At first, the concentration of DOC decreases sharply and reaches a value less than 2 mg/L from 30 to 360 minutes (6 hours), with the remaining DOC in the sample ranging from 0.68 to 1.6 mg/L, corresponding to a treatment efficiency of 74.1% to 89.0%. This result shows advantages over the DOC adsorption effect of aluminium (< 40% DOC), FeCl₃ (< 60% DOC) and heated aluminium oxide particles (about 40% DOC) [16]. After that, the adsorption capacity of the material in the column decreases as the DOC concentration measured in the effluent after 6 hours begins to increase, which is more than 4 mg/L after 14 hours and more than 5 mg/L after 18.5 hours. This occurrence is due to the fact that the magnetite Zn–Al LDH used is unchanged but the amount of DOC needed to be removed increases. After 20 hours, the material in the column almost loses its adsorption capacity, since the measured DOC concentration ranges from 5.79 mg/L to 6.11 mg/L, approximately to the initial DOC concentration.

For the empirical analysis, this study uses the linear adsorption equation of Oulman (1980) as follows:

\[
\ln \left( \frac{C}{C_0 - C} \right) = - \frac{K \times N \times x}{v} + K \times C_u \times t
\]  

where \( C_0 \) (mg/L) is the initial DOC concentration, \( C \) (mg/L) is DOC concentration after \( t \) (h) of adsorption, \( K \) (L/mg-h) is adsorption co-efficient, \( N \) (mg/L) is magnetite Zn–Al LDH adsorption capacity, \( v \) (cm/h) is the influent flow through the column model and \( x \) (cm) is the height of the material placed inside the column.

The correlation between \( \ln \left( \frac{C}{C_0 - C} \right) \) and \( t \) is highlighted as \( R^2 = 0.9222 \), resulting in DOC removal efficiency in continuous flow model reaches 50.54% and the adsorption capacity of the current model is 8.12 mg/g. Meanwhile, in the research of Johnsen (2011) on DOC removal using poorly podzolized high latitude soil with a low Al and Fe content, its adsorption capacity is reported to be 0.25 mg/g [17], while that value in Kothawala’s research using a developed podzol only achieves 0.29 mg/g [18].

4 CONCLUSION

This study has successfully proven the ability of the state-of-the-art magnetite Zn–Al LDH material to adsorb organic matter in raw water bodies. pH affects the adsorption capacity of DOC in raw water samples. Empirical test has shown that the adsorption process is highly effective when the sample solution is adjusted to a pH value of 5 to 6. The adsorption capacity of DOC in water samples of Thu Duc water plant by static adsorption system is 22.47 mg/g. The adsorption efficiency of the column after 21 hours is 50.54%.

Although the DOC content in the raw water samples of Tan Hiep water plant and Thu Duc water plant is not high and can be eliminated after the coagulation stage, this study on the adsorption of DOC with magnetite Zn–Al LDH has shown positive results, proving the material can be used to treat water sources containing high dissolved organic content to indirectly prevent the formation of THMs and protect human health.

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REFERENCES


Ứng dụng vật liệu hydroxit lớp kép Zn – Al LDH - Magnetite trong việc loại bỏ chất hữu cơ trong nước cấp

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Tóm tắt—Trong nghiên cứu này, hỗn hợp hydroxit lớp kép (Zn-Al LDH) và Fe₃O₄ đã được tổng hợp thông qua phương pháp đồng kết tủa hóa học. Các mẫu nước thô của nhà máy nước Thủ Đức và Tân Hiệp cũng được thu thập và sử dụng làm đối tượng nghiên cứu khả năng hấp thụ chất hữu cơ hòa tan (DOC) của vật liệu. Kết quả nghiên cứu hấp thụ thực nghiệmDOC trong các mẫu nước thô của các nhà máy nước Thủ Đức và Tân Hiệp cũng cho thấy các quá trình hấp thụ đạt hiệu suất cao khi các dung dịch mẫu được điều chỉnh pH từ 5 đến 6. Sau 21 giờ, chất hấp thụ trong cột mất khả năng hấp thụ của nó và dung lượng hấp thụ liên tục của vật liệu đạt 8,12 mg/g.

Từ khóa—hấp thụ, loại bỏ chất hữu cơ, nước cấp, vật liệu hydroxit lớp kép Zn-Al LDH magnetite