Atrazine Adsorption Potential of Leonardite from Mae Moh Power Plant

A Rittirat¹, C Chokejaroenrat² and A Watcharenwong¹*

¹ School of Environmental Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand.
² Department of Environmental Technology and Management, Faculty of Environment, Kasetsart University, Bangkok 10900, Thailand.

*E-mail: w.apichon@sut.ac.th

Abstract. Leonardite is an immature coal from the power plant, which we obtained from Lampang province, Thailand. It is known to contain relatively high humic substance making it suitable as the soil conditioner in agricultural aspect and as an adsorbent. Our objectives were:

(1) to determine the leonardite physical and chemical properties (e.g., cation exchange capacity, organic matter content, and electron microscope imaging), and (2) to quantify the adsorption efficiency of atrazine from the soil. We used varied amount of leonardite ranging from 0.05 to 1.60 g to adsorb 8 mg L⁻¹ of atrazine from aqueous solution in a batch experiment. This experiment was achieved within 48 hours so that the equilibrium time and isotherm parameters can be determined. The uncarbonized leonardite characteristic revealed that it could adsorb atrazine as its surface possesses mesopore type, relatively high cation exchange capacity (59.89 cmol Kg⁻¹), and high organic matter of 21.62 %. The isotherm study showed the equilibrium time of 24 hours and adsorption isotherm was Langmuir with q_max of 3.9683 mg g⁻¹. This study provides proof that leonardite used in the agricultural field can also be useful to adsorb atrazine and simultaneously slow the percolating process of atrazine before contaminating groundwater.

1. Introduction
Leonardite is an immature coal [1]. It is an oxidized form of the lignite coal and the deposition of humus [2,3]. Leonardite consists of inorganic and humic substances around 40-80 % [1]. The humic substances in leonardite can be used as a soil conditioner to promote the plant growth [4]. Humic acid contained organic functional group such as hydroxyl, phenol and carboxyl, its affected for cation exchange in aqueous solution [2]. Moreover, leonardite can be used as the adsorbent for the organic and inorganic substance adsorption's studies. For example, some research group used carbonized-leonardite to remove the congo red in aqueous solution [3]. Some studies related to the removal of As (V) from aqueous solution by leonardite mixing a ferric ion (Fe-leonardite) and the leonardite mixing a clinoptilolite to removal Zn (II) ions from aqueous solution [5]. However, no such feasibility for the adsorption of herbicide as atrazine solution by leonardite have been reported.
Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is commonly used for a pre- and post-emergent herbicides to control broadleaf weeds. Similarly, atrazine is normally used as herbicides for sugar cane and corn crops. Atrazine has high mobility and can contaminate surface and groundwater by runoff. Moreover, atrazine might be a human carcinogenic compound [6]. The regulation of European Commission No.396/2005 and United State environmental protection agency (US. EPA) has banned atrazine for the agriculture. The maximum atrazine levels in drinking water of these two regulations were at 0.1 ppb and 3 ppb respectively [6, 7]. Nowadays, atrazine has been intensively used in Thailand. Consequently, atrazine removal from the environment has essential importance for the protection of public health and water source.

The aim of this study was to investigate the atrazine adsorption using leonardite. The experiment starts from the characterization of leonardite adsorbent. The characteristic of leonardite such as the elements and components, cation exchange capacity (CEC), organic matter, pore size, and surface area were analyzed. Batch adsorption experiment was conducted to investigate the equilibrium time and batch adsorption isotherm. Throughout the studies, the atrazine solution has been analyzed by high-performance liquid chromatography (HPLC).

2. Methodology

2.1. Preparation and characterization of leonardite
The leonardite sample obtained from Mae Moh power plant in Lampang province, Thailand. The leonardite was dried in an oven at 105 °C, 3 hours for moisture removal. Then it was crushed (GmbH D-42781, Retsch HAAN Germany) and sieved under 150-250 μm (60-100 mesh). Then, the leonardite was kept in a desiccator before use in the experiments. Elements contained in leonardite was characterized by X-ray fluorescence spectrometry (XRF) at 50 KV (XGT-5200, Horiba). The crystalline structure was observed by X-ray diffractometer (XRD) (XRD D2 Phaser, Bruker). The elemental composition (carbon, hydrogen, oxygen, nitrogen, and sulfur) was analyzed by element analyzer (628S: CHN628 LECO). Scanning electron microscope (JSM-6010, JEOL) was used to analyze the morphologies of leonardite. Laser scattering particle size distribution analyzer (LA-950V2, Horiba) was determined surface area and pore size, this method applied by N₂ gas adsorption analysis and degradation at 110 °C for 11 hours.

2.2. Atrazine adsorption experiments
Atrazine (Chem service) with a purity of 98.1 % was used as obtained. The stock solution of atrazine 1,000 mg/l was prepared in DI water (18 mΩ).

2.2.1. The equilibrium time of atrazine adsorption. The atrazine concentrations of 1.0, 2.0 and 4.0 mg/l were studies. Leonardite of 0.4 g was added to 25 ml of each atrazine concentration into EPA vials. The vials were shaken in a shaker at 200 rpm. Samples were taken at various contact time at 0-48 hours. Adsorption experiments were performed at room temperature. Then, the samples were measured the atrazine concentrations by HPLC.

2.2.2. Batch adsorption isotherm experiments. Batch adsorption isotherm was using 0.05, 0.1, 0.2, 0.4, 0.8 and 1.6 g of leonardite in 25 ml of 8 mg/l atrazine solutions. Adsorption experiments were
performed at room temperature. Samples were collected after 24 hours of adsorption. The samples were determined atrazine concentrations by HPLC.

2.3 Analysis of atrazine concentration by HPLC
The collected sample was spun at 14,000 rpm for 10 min by centrifuge machine. Afterward, the separation of the adsorbent from atrazine solution was performed using nylon filter 0.45 µm. Adsorption experiments were conducted at room temperature. Determinations of atrazine concentration were carried out by HPLC instrument (Agilent 1260 infinite, USA). The UV/Vis detector was set at 220 nm. The column used was a C-18 ACE (5 µm, 4.6 x 250 nm). The mobile phase was acetonitrile: DI water (60:40) and the injection volume was set at 1 ml/min.

3. Results and discussion

3.1 characteristics of Leonardite
The results from chemical characterization of leonardite found that, the pH of leonardite is 2.85 (in H₂O) indicated high acidity. The pH affected the ion exchange capacity on the adsorbent. Ausavasukhi et al.[2] reported that, the efficiency of organic adsorption (congo red; CR) by leonardite was increased at mostly acidity. The organic substance adsorption was decreased at pH increasing. Because the hydroxide ion (OH⁻) and carboxyl group (−COOH) on the surface of leonardite can disturb the anionic adsorption of the functional groups of atrazine [2, 8, 9]. Leonardite consists of carbon around 16.54 % and oxygen around 26.67 % as indicated by XRF analysis. The XRD result showed the major phases of leonardite, it has most of the quartz (SiO₂) and gypsum (CaSO₄ · 2H₂O). Leonardite has a cation exchange capacity (CEC) of 59.98 %. The high CEC value imply that this material has high organic matter. Hence, it affected the adsorption of atrazine on negative site. Moreover, leonardite consists of humic acid and nutrient which can be used as a soil conditioner. The BET surface area and pore diameter of leonardite were 13.59 m²/g and 21.65 nm respectively. Leonardite was classified as mesoporous material (2.50 nm) [10]. These pores serve as the path for the pollutant molecule move into a small pore of the particle. The pictures of leonardite were shown in the figure 1.

![Figure 1. The leonardite at (a) Real picture of leonardite (b) SEM image of leonardite at 50 kx](image-url)

3.2 Equilibrium time of adsorption
The equilibrium time of the atrazine adsorption on leonardite was around 24 hours. The adsorption efficiencies from 24 hours to 48 hours were similar.
3.3 Adsorption isotherm

The adsorption isotherm studies were conducted with 8 mg/l of atrazine concentration, and the amount of leonardite was varied at 0.05, 0.1, 0.2, 0.4, 0.8 and 1.6 g. All experiments were shaken with 200 rpm at room temperature for 24 hours. The Langmuir isotherm is practical to monolayer adsorption and homogeneous surface. While the Freundlich isotherm is widely for the surface heterogeneous and assumes to multilayer capacity [6]. The linear of Langmuir and Freundlich isotherms was expressed as equation (1) and (2), respectively.

\[ 1/q_e = 1/(q_{max}K_LC_e) + 1/q_{max} \]  

(1)

Where \( q_{max} \) is the maximum adsorption capacity (mg/g) and \( K_L \) is the Langmuir constant (L/mg), determined from the slope and intercept of linearized plot of \( 1/q_e \) (where \( q_e \) is the amount of atrazine adsorbed by leonardite at equilibrium; mg/g) and \( 1/C_e \) (where \( C_e \) is concentrations of atrazine at equilibrium in solution; mg/L).

\[ \log q_e = \log K_f + 1/n \log C_e \]  

(2)

Where \( K_f \) is the Freundlich adsorption equilibrium constant (mg/g) and \( n \) is a constant indicative of adsorption intensity. Moreover, \( R^2 \) value has asserted the adsorption isotherm in a linear question. For the results followed a both of Langmuir and Freundlich isotherm were shown in Figure 2. The parameters of adsorption isotherm were shown in table 1.

![Figure 2. Adsorption isotherm of atrazine on leonardite by (a) Langmuir model and (b) Freundlich model](image)

| Table 1 | Langmuir and Freundlich isotherm equation for atrazine adsorption by leonardite |
|---------|----------------------------------------------------------------------------------|
| Langmuir isotherm              | Equation | \( R^2 \) | \( q_{max} \) (mg/g) | \( K_L \) (L/mg) | Freundlich isotherm |
| Y = 14.1539x + 0.2520          |          | 0.9917    | 3.9683               | 0.0178            | Y = 0.9923x - 1.1723 |
|                                  |          |           |                      |                   | \( R^2 \) | \( n \) | \( k_f \) |
|                                  |          |           |                      |                   | 0.9674 | 1.0077 | 0.0673 |

The atrazine adsorption isotherm by leonardite at equilibrium conditions followed a both of Langmuir and Freundlich isotherm. The maximum Langmuir adsorption capacity is 3.9683 mg/g, which is a monolayer of surface area to limit of molecules to adsorb atrazine. The mechanism of atrazine adsorption may be deepened on the leonardite’s surface and its binding with the functional group of atrazine [9]. Likewise, the atrazine adsorption depended on the pore size on the adsorbent, because the molecular size of atrazine is on around 0.80-0.85 nm [6]. So the mesopore of leonardite (2-50 nm) rendered an atrazine solution pass through into the inner surface of leonardite [7]. Moreover, hydroxyl and a carboxylic group from humic compounds in leonardite play a key role in atrazine adsorption [11]. Therefore, the functional group and surface area affected by atrazine adsorption by leonardite.
4. Conclusion
This study has shown that the leonardite can adsorbed atrazine from aqueous solution. The equilibrium time of adsorption was around 24 hours. The Langmuir adsorption isotherm fitted well with atrazine adsorption by leonardite. The main factors affected atrazine adsorption by leonardite are the pore diameter and specific surface area. Moreover, the humic compounds in leonardite were dominated by the atrazine adsorption. Finally, leonardite could relieve the herbicides contaminate to the surface and groundwater by runoff. Moreover, the utilization of leonardite as the soil conditioner in agriculture area could be possible.

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