

Study of atrazine removal by an adsorbent synthesised by water hyacinth

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Abstract. In this work, water hyacinth was selected as a raw materials for synthesising the activated carbon used for removing atrazine, one of the most famous herbicides used in Thailand, from water. Three different treating methods were performed in order to attain the best adsorbent; untreated (AC), HCl-treated (HCl-AC) and NaOH-treated (NaOH-AC) activated carbons. After pyrolysis, NaOH-AC became ash, so it was not suitable for using as an adsorbent. Among these, HCl-AC was the best adsorbent for removing atrazine from water because of its highest surface areas. The adsorption experiments using AC and HCl-AC as the adsorbents confirmed that the adsorption efficiency of HCl-AC was higher than that of AC. In addition, the adsorption isotherm of HCl-AC was investigated by varying the atrazine initial concentration in the range of 3-15 ppm. The results best fitted with Langmuir isotherm that means this adsorption phenomenon was chemisorption with the maximum adsorbent capacity of 24.510 mg/g, Langmuir isotherm constant of 10.462 L/mg and the separation factor of 0.006 indicating that the equilibrium sorption of atrazine by HCl-AC was favourable.

1 Introduction

Thailand is an agricultural country where exports various kinds of agricultural products. Therefore, there is the using of some herbicides for producing high-quantity agricultural products. Thailand imports the large amount with high value of herbicides between 2010-2015 [1]. Atrazine, ($C_8H_{14}ClN_5$) is the Thailand top ten imported organochloride herbicide [2], is used to control weeds in farms and crop land sand for example corn, sugarcane, or millet farm. Due to their extensive usage and its long half life about 13-261 days and more than 200 days in soil and water resources, respectively [3]. This affects the contamination in surface water and ground water of Thailand [4]. Atrazine also affects to frog mutation [5], ecology [4] and human health [6]. Therefore, because of its hazard, it is necessary to remove atrazine from water resources.

The examples of atrazine removal techniques from water are incineration, reverse osmosis, electrodialysis, chemical degradation and etc. Nevertheless, all of these techniques are costly and produce corrosive and toxic gases [7]. Adsorption is a simply attractive method since the atrazine is adsorbed on the adsorbent's surface. The common adsorbent is an activated carbon because of its high surface area and porosity. However, activated carbon is an expensive material thus it is necessary to develop a low cost effective carbon that can be used to remove the contaminant from water. One property affecting the adsorption capacity is porosity which

depends on nature of raw material and activation method. Since Thailand is an agricultural country, the large amount of agricultural wastes exist and be many studies for producing an effective activated carbon e.g. coconut shell, watermelon peel, rice straw and etc. One of the waste causing many problems in Thailand is a water hyacinth (*Eichhornia crassipes*) that is a free-floating perennial aquatic plant which can propagate and grow easily. The large amount of water hyacinth makes a rotten water because oxygen cannot dissolve into water, blocks waterways, affects both navigation and drainage, and increases siltation and flooding probability.

In the consequence, this study aims to prepare a low cost activated carbon from water hyacinth for atrazine adsorption. This means that this study will change waste material (water hyacinth) to be a valuable material. As complex structure of atrazine, chemical and physical treatments are needed to increase the porosity of water hyacinth. The effect of different kinds of activated carbon preparation methods on adsorption is investigated. In addition, the adsorption isotherm of the best adsorbent prepared in this work was determined in order to understand the phenomenon of atrazine adsorption.

2 Experiments

2.1. Dried water hyacinth preparation

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The stem of water hyacinth collected from the river was peeled, cleaned with water, chopped into pieces with the thickness of 0.2 cm and dried under the sunlight for 3 days. After that, water in the stem pieces was removed by baking at 105°C until the weight was constant. Then, it was cooled down to room temperature and treated by 3 different methods as follow.

2.2 Treatment methods

1) Untreated method

The dried water hyacinth was pyrolysed at 500 °C under N₂ in the furnace for 1 h and, then the activated carbon was obtained. After cooling to room temperature, the activated carbon was ground and sieved to be 200-250 mesh-size. This activated carbon will be abbreviated as AC in the following.

2) HCl-treated method

The 10 g of dried water hyacinth was left in 1 L of 1 M HCl solution for 2 days. After that, water hyacinth was separated from solution by filtration and washed by distilled water until the pH of washed water was neutral. Then, it was baked at 105 °C for 2 days and pyrolysed at 500 °C under N₂ in the furnace for 1 h. After cooling to room temperature, the activated carbon was ground and sieved to be 200-250 mesh-size. The activated carbon prepared from this method is called HCl-AC.

3) NaOH-treated method

The activated carbon attained from this method is called NaOH-AC. Its preparation was similar to HCl-AC, but the chemical used for treatment was NaOH instead of HCl.

2.3 Material characterisations

The adsorbents prepared from 3 different treating methods mentioned above were characterised by Brunauer–Emmett–Teller (BET) method in order to observe the surface areas, pore volumes and pore diameters and CHNS Analysis for determining the compositions of the adsorbents.

2.3 Adsorption isotherm study

The adsorption isotherm determination was performed by batch test. The 200-mL of atrazine with the various initial concentrations in the range of 3-15 ppm was prepared and stirred at the agitation speed of 150 rpm. Then, 0.1 g of adsorbent was added into atrazine solution. Samples were taken at appropriate time intervals and atrazine concentration of the samples was determined by using Gas Chromatography-Mass Spectroscopy (GC-MS) with HP-5 method.

3 Results and discussion

3.1. Material characterisations

After pyrolysis of water hyacinth treated by NaOH, this material became ash. This was probably because NaOH

could remove more lignin than HCl [8], so the amount of NaOH-treated water hyacinth pyrolysed was less than that of other treated methods. Due to high temperature of pyrolysis, most of NaOH-treated water hyacinth was therefore changed into ash. Thus, NaOH-AC was not further studied in this work.

The carbon percentages (%C), surface areas and pore diameters of AC and HCl-AC characterised by BET and CHNS Analysis are shown in Table 1. It can be seen that HCl treatment was able to improve the characteristics of the adsorbent, in terms of both %C, surface area and pore diameter, comparing with untreated method. Although, the pore diameter of HCl-AC was smaller than that of AC, but it was still bigger than the size of atrazine (10.36 Å) [9], so, among these, HCl-AC should be the best adsorbent for atrazine removal.

Table 1. Characteristics of the adsorbents

| Adsorbents | %C | Surface area (m ² /g) | Pore diameter (Å) |
|------------|--------|----------------------------------|-------------------|
| AC | 38.921 | 160.4 | 80.94 |
| HCl-AC | 71.192 | 436.0 | 29.01 |
| NaOH-AC | Ash | | |

Batch adsorptions by AC and HCl-AC with the atrazine initial concentration of 12 ppm were performed in order to confirm the hypothesis that HCl-AC was the best adsorbent in this work. The results are shown in Fig. 1. It can be seen that the atrazine concentrations in solutions decreased with time as a result of the adsorption process. However, time to equilibrium of AC was about 4 h that was shorter than that of about 5 h of HCl-AC. Furthermore, the remaining atrazine concentration in solution at equilibrium of the batch used HCl-AC as an adsorbent was lower than that of AC. That means the adsorption capacity of HCl-AC was higher than that of AC. These, both time to equilibrium and capacity, confirmed that HCl-AC was the best adsorbent because HCl treatment was able to improve the characteristics of the activated carbon which directly affected its adsorption efficiency.

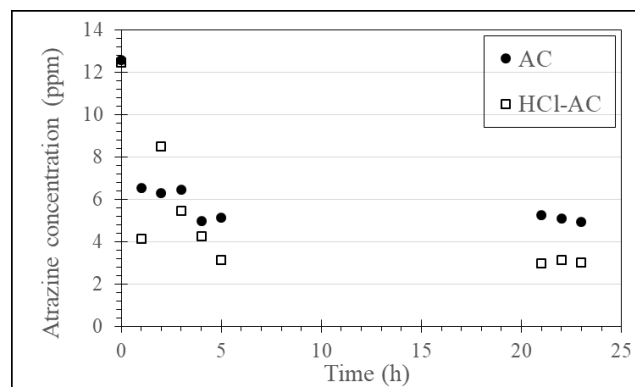


Fig. 1. The concentration of atrazine in solution with time during adsorption by AC and HCl-AC.

3.2. Adsorption isotherm

The atrazine adsorption isotherm by HCl-AC was investigated by varying the atrazine initial concentrations of 3, 6, 9, 12 and 15 ppm. For the adsorption of solution with the initial concentrations of 3 and 6 ppm, the adsorbent could adsorb all atrazine in solution, so only the results of 9, 12 and 15 ppm of initial concentrations were considered. The adsorption capacities at equilibrium were observed and fitted with 3 isotherm models [10-13] that were Langmuir isotherm (Eq. 1) assuming that the adsorption phenomenon is chemical adsorption and the maximum sorption corresponds to the saturated monolayer of adsorbate on adsorbent surface, Freundlich isotherm (Eq. 2) assuming that the adsorption is physical adsorption with multilayer of adsorbate on adsorbent surface and Temkin isotherm (Eq. 3) taking into account the effect of indirect interaction between adsorbate molecules and assuming that the heat of adsorption of all molecules in the layer decreases linearly due to the increasing of surface coverage. The linearised forms of Langmuir, Freundlich and Temkin isotherms were formatted as shown in Eqs. 4-6, respectively, and the fitted graphs are shown in Fig. 2.

Langmuir isotherm equation:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

Freundlich isotherm equation:

$$Q_e = K_F C_e^{1/n} \quad (2)$$

Temkin isotherm equation:

$$Q_e = \frac{RT}{K_T} \ln(A_T C_e) \quad (3)$$

Linearised form of Langmuir isotherm equation:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad (4)$$

Linearised form of Freundlich isotherm equation:

$$\log Q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (5)$$

Linearised form of Temkin isotherm equation:

$$Q_e = \frac{RT}{K_T} \ln A_T + \frac{RT}{K_T} \ln C_e \quad (6)$$

where

- Q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g)
- Q_m = the adsorption capacity (mg/g)
- C_e = the equilibrium concentration of adsorbate (mg/L)
- K_L = Langmuir isotherm constant (L/mg)
- K_F = Freundlich isotherm constant (mg/g)
- K_T = Temkin isotherm constant
- n = adsorption intensity
- A_T = Temkin isotherm equilibrium binding constant (L/g)
- R = Gas constant (J/mol K)
- T = Absolute temperature (K)

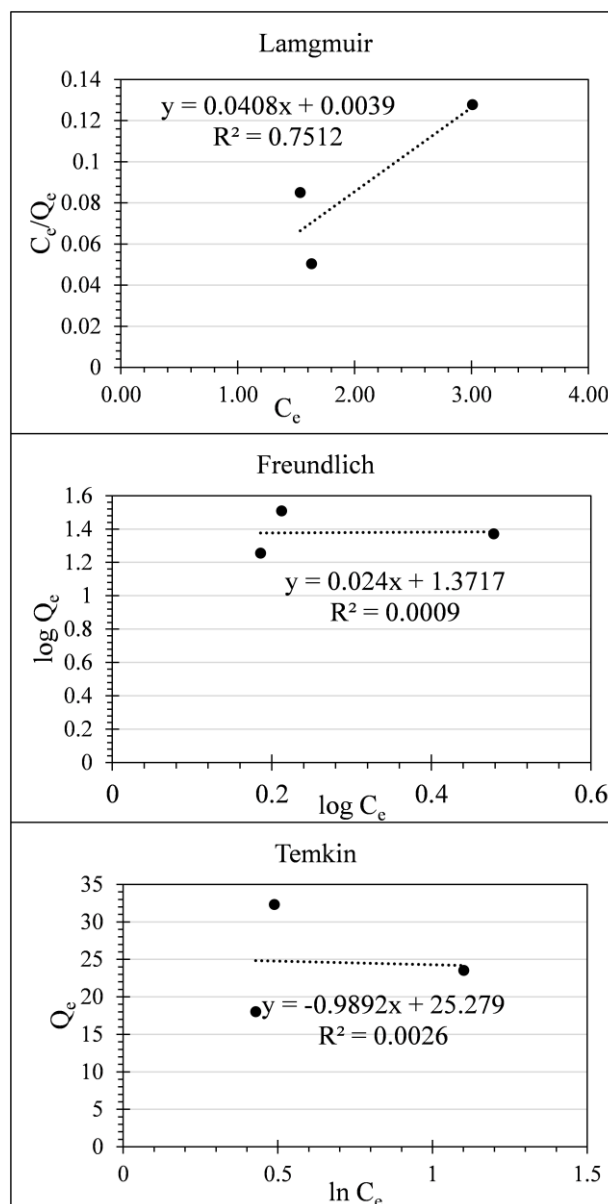


Fig. 2. (a) Langmuir, (b) Freundlich and (c) Temkin plotted of adsorption isotherms in the atrazine adsorption process using HCl-AC as an adsorbent.

Fig. 2. shows that Langmuir isotherm model best fitted with adsorption results with R^2 of 0.7512. Even the R^2 value was not high but it was the highest value comparing with those of other isotherm models. This means that the adsorption phenomenon of atrazine by HCl-AC was chemisorption revealing that there was a chemical interaction between atrazine and the homogeneous active site of HCl-AC.

The adsorption parameters in Langmuir equation which are Q_m and K_L can be calculated by fitting the equation in linearised form (Eq. 7) [10-11]. The slope and y-intercept of the graph represent $1/Q_m$ and $1/Q_m K_L$, respectively. It can be found that the adsorption capacity (Q_m) of HCl-AC was 24.510 mg/g and Langmuir isotherm constant (K_L) which is related to the energy of adsorption was 10.462 L/mg.

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad (7)$$

The essential characteristics of Langmuir isotherm can be expressed in terms of a separation factor (R_L), so-called equilibrium parameter, which is a dimensionless constant given by Eq. 8.

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

where C_0 is the highest initial concentration of adsorbate in ppm.

The value of R_L indicates the nature of adsorption to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [11-12]. In this work, the value of R_L was 0.006 indicating that the adsorption of atrazine by HCl-AC was favourable.

4 Conclusions

1). The best treatment method for synthesising the activated carbon adsorbent was HCl treatment, since the characteristics, surface area and %C, of HCl-AC was improved comparing with those of AC. Although, the pore diameter of HCl-AC was finer than that of AC, but HCl-AC was still able to adsorb atrazine because its pore diameter was larger than the size of atrazine molecule. For NaOH-AC, ash presented after pyrolysis that means this treatment method was not suitable for synthesising adsorbent.

2). The adsorption experiments using AC and HCl-AC as the adsorbents showed that the adsorption capacity of HCl-AC was higher than that of AC. This confirmed the characterisation results and indicated that HCl treatment can improve the characteristics of the adsorbent affecting the better performance of the material.

3). Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms were fitted with the experimental adsorption data of the batch using HCl-AC as an adsorbent to describe the adsorption phenomenon. Among these, Langmuir isotherm best fitted with the R^2 of 0.7512. From the calculation, the adsorption capacity

(Q_m) of HCl-AC was 24.510 mg/g, Langmuir isotherm constant (K_L) which is related to the energy of adsorption was 10.462 L/mg and the dimensionless separation factor (R_L) was 0.006 indicating that the adsorption of atrazine by HCl-AC was favourable.

References

- Office of Agricultural Economics. (2016). [Online]. Available: http://www.oae.go.th/ewt_news.php?nid=146. [Accessed: 18-Nov-2017].
- A. Tawatsin, U. Thavara, P. Siriyasatien, Medical Research Archives, 3 (2015).
- U.S.Department of Health and Human Service Agency for Toxic Substances and Disease Registry. (2003). [Online]. Available: <https://www.atsdr.cdc.gov/toxguides/toxguide-153.pdf>. [Accessed: 18-Nov-2017].
- M. Graymore, F. Stagnitti, G. Allinson, Environmental International **26**, 7-8, 483-495 (2001).
- T.B. Hayes, V. Khoury, A. Narayan, M. Nazir, A. Park, T. Brown, L. Adame, E. Chan, D. Buchholz, T. Stueve, S. Gallipeau, Ecology **107**, 10, 4612-4617 (2010).
- Pesticide action network.). [Online]. Available: <http://www.panna.org/resources/atrazine> [Accessed: 18-Nov-2017].
- R.K. Pathak, A.K. Dikshit, International Conference on Life Science and Technology IPCBEE **3**, 19-22 (2011).
- M. Badiei, N. Asim, J.M. Jahim, K. Sopian, APCBEE Procedia **9**, 170-174 (2014).
- S.S. Chen, J.S. Taylor, L.A. Mulford, C.D. Norris, Desalination **160**, 2, 103-111 (2004).
- X. Chen, Information **6**, 14-22 (2015).
- B.H. Hameed, J.M. Salman, A.L. Ahmad, Journal of Hazardous Materials **163**, 121-126 (2009).
- A.O. Dada, A.P. Olalekan, A.M. Olatunya, O. Dada, IOSR Journal of Applied Chemistry **3**, 1, 38-45 (2012).
- J.M. Salman, V.O. Njoku, B.H. Hameed, Chemical Engineering Journal **174**, 41-48 (2011).