Removal of Atrazine from Water Using Oil Palm Shell Based Adsorbents: Equilibrium and Kinetic Study

H. T. Moh¹, Ivy A. W. Tan², and Leonard L. P. Lim³

Abstract: Adsorption using granular activated carbon (GAC) in a permeable reactive barrier (PRB) has been proven in inhibiting the further spread of contaminant plumes in groundwater. GAC synthesized from oil palm shell was chosen for groundwater remediation in this study due to the low operation cost using the adsorption process. In this study, GAC synthesized from oil palm shells were used as adsorbent to adsorb atrazine from water. This study involved a series of batch experiment to determine the adsorption equilibrium and kinetics of adsorbent. The batch experiment was conducted by shaking conical flasks containing 0.6 g GAC in 300 mL solution with initial atrazine concentrations of 5, 10, 20 and 30 mg/L at 180 rpm at 30 ± 2 °C. The GAC showed more than 95% of atrazine removal in all the batch experiments. The adsorption kinetic study showed that the adsorption of atrazine is of physisorption as the experimental data is fitted better to the pseudo-first-order model than the pseudo-second-order model. In the adsorption isotherm study, the adsorption of atrazine onto GAC was better described by the Freundlich model which indicated multilayer adsorption on the heterogeneous surface of the adsorbent. The atrazine adsorption capacity of the GAC was 15.132 mg/g, which was higher than that using the activated carbon synthesized from waste charcoal (13.947 mg/g). This study shows that there is a potential for GAC to be used for remediating groundwater contaminated by pesticides.

Keywords: granular activated carbon, atrazine, batch experiment, equilibrium study, kinetic study

I. INTRODUCTION

PESTICIDES are the major contribution in today’s intensive agriculture [1]. The use of pesticides beyond maximum residue level (MRL) in agricultural sectors could cause contamination of groundwater and surface water resources due to their leaching and runoff losses [1]-[4]. Pesticides were persistence in groundwater due to its resistance to natural degradation processes and have been classified as persistent organic pollutants (POPs) [3], [5], [6]. POPs have been known as an increasing problem in water supplies [6]. Groundwater contamination by pesticides can negatively affect the human reproductive systems if consumed as it is being directly used for drinking purpose [1], [2]. Therefore, there is a need to remediate the groundwater due to its severe impact.

There are various technologies available to remove pesticides from groundwater such as pump-and-treat and air sparging [7]. Some of the technologies have to combine together such as air sparging and soil vapor extraction in order to reach the desire clean up level and this will increase the remediation cost. In addition, the efficiency of those technologies was limited by soil heterogeneity [8], [9]. However, the groundwater remediation which is not affected by soil heterogeneity is the permeable reactive barrier (PRB). PRB is a trench with used of adsorbent as reactive material to inhibit migration of contaminants plume [10], [11]. Adsorption process had been used in PRB to remove pesticides in groundwater [10]-[12].

Adsorption is a physical process involving the attraction of contaminant molecules onto the surface of the adsorbent [7]. Adsorption technology such as PRB was being widely used presently to remove pesticides from the groundwater due to high removal efficiency and does not produce harmful by-products [13]-[15]. The commercial industrial adsorbent is granular activated carbon (GAC) which is widely used adsorbent in removing organic contaminants from water [4], [16]. GAC were widely used in the treatment of wastewater due to it advantageous of physiochemical properties including excellent mechanical strength, chemical stability in different media and distributing large pore size in addition to its wide specific surface area [4]. The treatments by using GAC as adsorbent had successfully removed the pesticides of aldrin, ametryn and applaud by 98 %, 75 % and 80 %, respectively [17].

Adsorption is suitable for adsorb the contaminants from groundwater due to slow groundwater flow (33 m/year) [18]. This means that long residence time and slow migration of contaminant groundwater to flow through the PRB. There is a potential use of GAC synthesized from oil palm shell for groundwater remediation due to the low operation cost using an adsorption process. Adsorption process is considered better due to easiness of operation, simplicity of design and can remove different contaminants.
type of pollutants [19]. Some of the adsorbents synthesized from agriculture wastes have shown promising results in adsorption of contaminants from water. Adsorbent derived from coconut husk activated carbon and fly ash adsorbed 434.78 mg/g methylene blue and 27.9 mg/g phenol, respectively [20], [21].

Therefore, adsorbent and GAC synthesized from the oil palm shell is used as the raw material in this study due to the significant amount of oil palm waste in Sarawak, being a major contributor to Malaysian oil palm production of 12.8 % (2.18 million tonnes) in 2011, and is projected to increase [22]. The use of oil palm shell can help to reduce the amount of oil palm wastes to be disposed, therefore contributing to environmental protection. In batch experiment, the adsorption capacity and efficiency of the adsorbent was tested on removing atrazine from the water.

II. MATERIAL AND METHODS

Adsorbent

Commercially available GAC synthesized from oil palm shell as adsorbent was obtained from Bravo Green Sdn. Bhd. and is located at Kota Samarahan. The size for this GAC used was at ranged from 1.68 to 3.36 mm (US mesh – 6 × 12).

Target Contaminant

Atrazine (Fluka 45330) was used to represent the pesticides in this study. The initial concentrations of atrazine in this study were 5, 10, 20 and 30 mg/L.

Batch Experiment

The batch experiment had been carried out to determine the adsorption capacity of the GAC synthesized from oil palm shells. Adsorption capacity is conducted by using 0.6 g of GAC with 300 mL of atrazine solution in conical flask with different concentrations. The various initial concentrations of atrazine in this study were 5, 10, 20 and 30 mg/L. The conical flasks then were placed into the refrigerated incubating shaker (Thermo Scientific) at temperature (30 ± 2 °C) for 25 hours at 180 rpm in order to achieve equilibrium. The initial and final pH of the solutions was measured by using pH meter (Oakton® Waterproof Eco TestrTM pH 2).

Sample Analysis

For the sample analysis, the samples were filled into 4 mL quartz cell cuvette. Then, the quartz cell cuvette was placed into UV-visible spectrophotometer to analyze. The temperature of the analyzed was at 22 ± 2 °C. Methanol was added into the solution to emulsify the atrazine in water samples to analyze. Methanol is an organic solvent and will break up the pesticides into smaller droplets so that it is easier to be detected.

III. RESULTS AND DISCUSSION

Effect of Initial Concentration of Atrazine on Adsorption Equilibrium

Figure 1 shows the effect of various initial concentrations of atrazine on the adsorption of atrazine by the GAC at 30 °C. The atrazine adsorption was fast at the initial stages of the experiment but become slower when nearing to the equilibrium point. In all the experiments, the equilibrium point occurred about 240 minutes after the experiment started, whereby the curve reached a plateau. The adsorption of atrazine reached a state of dynamic equilibrium in which there was no change in the concentration of atrazine. The equilibrium concentrations (Cₑ) were 0.079, 0.142, 0.122 and 0.428 mg/L for initial atrazine concentrations of 5, 10, 20 and 30 mg/L, respectively.

The amount of atrazine adsorbed at the equilibrium time show that the maximum adsorption capacity of the GAC under the operating condition applied. Adsorption capacity of the GAC was due to the number of vacant surface sites were available for adsorption. During the initial stage, atrazine adsorption was fast because there was large number of vacant surface of GAC were available for adsorption. Atrazine molecules moved through the firm surrounding of the external surface of GAC, the molecules then diffuse from the external surface into the pores of the GAC. At final stage, the molecules are adsorbed on the active sites located at the internal surface within the pores and the atrazine adsorption become equilibrium because remaining vacant surface of GAC were difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases [23], [24].

In this study, the adsorption at equilibrium, qₑ, increased from 2.963 to 15.132 mg/g with an increase in initial concentration from 5 to 30 mg/L. When the initial atrazine concentration was increased, the mass transfer force would become larger and resulting in higher atrazine adsorption [23].
Adsorption Kinetic Studies

There are two models used to study the rate of adsorbate uptake on GAC and it controls the equilibrium time [23]. Pseudo-first-order (Equation (1)) [25] and pseudo-second-order (Equation (2)) [26] kinetic models were used to evaluate the mechanism of the adsorption process and study the kinetics of the adsorption process.

\[
\ln \left( q_e - q_t \right) = \ln q_e - k_1 t \\
\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{1}{q_e} t
\]  

Where \( q_e \) (mg/g), \( q_t \) (mg/g) are amounts of atrazine adsorbed onto activated carbon per unit mass of activated carbon at equilibrium and at any time \( t \) (min), respectively. \( k_1 \) (1/min) and \( k_2 \) (g/mg min) are the rate constants of pseudo-first-order and pseudo-second-order adsorptions, respectively. The linear plot of pseudo-first-order is shown in Figure 2 and the linear plot of pseudo-second-order is as shown in Figure 3, the two plots are more likely to evaluate the mechanism of the adsorption process.

Table 1 shows the data for pseudo-first-order and pseudo-second-order kinetic. The linear plot of \( \ln (q_e - q_t) \) versus \( t \) in Figure 2 gave the slope of \( k_1 \) and intercept of \( \ln q_e \). The values for \( q_e \), \( k_1 \) and correlation coefficient, \( R^2 \) obtained from the graph for adsorption of atrazine using GAC at 30 °C were recorded in Table 1. This procedure was done to determine the behavior over the whole range of adsorption. The values between the experimental \( q_e \) and the calculated \( q_e \) in Table 1 were quite similar. Moreover, the correlation coefficient, \( R^2 \) values for the first-order kinetic model were almost equal to unity for all atrazine concentrations. The correlation coefficient, \( R^2 \) values were in the range from 0.811 to 0.989 for atrazine initial concentration of 5 to 30 mg/L. Hence, this shows the applicability of the first-order kinetic model to describe the adsorption process of atrazine using GAC.

<table>
<thead>
<tr>
<th>Initial Conc. (mg/L)</th>
<th>( q_e ) exp. (mg/g)</th>
<th>% Removal</th>
<th>Pseudo-first-order parameter</th>
<th>Pseudo-second-order parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_e ) calc. (mg/g)</td>
<td>( k_1 ) (min(^{-1}))</td>
<td>( R^2 )</td>
<td>( q_e ) calc. (mg/g)</td>
</tr>
<tr>
<td>5</td>
<td>2.963</td>
<td>98.684</td>
<td>6.586</td>
<td>0.029</td>
</tr>
<tr>
<td>10</td>
<td>5.275</td>
<td>98.672</td>
<td>6.469</td>
<td>0.016</td>
</tr>
<tr>
<td>20</td>
<td>9.315</td>
<td>99.349</td>
<td>10.892</td>
<td>0.012</td>
</tr>
<tr>
<td>30</td>
<td>15.132</td>
<td>98.605</td>
<td>15.180</td>
<td>0.009</td>
</tr>
</tbody>
</table>

The linear plot of \( t/q_t \) versus \( t \) in Figure 3 gave the slope of 1/\( q_e \) and intercept of 1/(\( k_2 q_e^2 \)). The values for \( q_e \), \( k_1 \) and correlation coefficient, \( R^2 \) obtained from the graph for adsorption of atrazine using GAC at 30 °C were recorded in Table 1. This procedure was done to determine the behavior over the whole range of adsorption. The values between the experimental \( q_e \) and the calculated \( q_e \) in Table 1 were quite different. Moreover, the correlation coefficient, \( R^2 \) values for the second-order kinetic model were relatively small. The correlation coefficient, \( R^2 \) values were in the range from 0.356 to 0.990 for atrazine initial concentration of 5 to 30 mg/L. Hence, this shows that the adsorption of atrazine using GAC is not a second-order reaction.
Adsorption Isotherms

There are two models used to explain the experimental data for the adsorption isotherms in this study. Adsorption isotherms are used to describe how the molecules of adsorbates interact with adsorbent surface. Langmuir (Equation (3)) [24] and Freundlich isotherms (Equation (4)) [24] were used to evaluate the type of adsorbent surface.

\[
\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \left(\frac{1}{Q_0}\right) C_e
\]  

(3)

\[
Q_0 \text{ (mg/g)} \text{ and } K_L \text{ (L/mg)} \text{ are Langmuir constants in relation to maximum monolayer adsorption capacity onto a surface with no transmigration of adsorbates in the surface [27], [28].}
\]

\[
\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e
\]  

(4)

\[K_F \text{ and } n \text{ are Freundlich constants in relation to adsorption capacity on a heterogeneous surface or surfaces supporting sites of varied affinity and how favourable the adsorption process assuming that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation, respectively [23], [27]. The slope of } 1/n \text{ is used to measure the adsorption intensity or surface heterogeneity which ranging between 0 and 1, the surface become more heterogeneous as the value close to zero [24]. The other important characteristic of Langmuir isotherm is a dimensionless constant, separation factor, } R_L, \text{ which can be calculated from the Equation (5) [24].}
\]

\[
R_L = \frac{1}{1 + K_L C_0}
\]  

(5)

Where \(K_L\) is the Langmuir constant and \(C_0\) is the highest dye concentration (mg/L). The value of \(R_L\) can indicate the type of isotherm to be either unfavorable (\(R_L > 1\)), linear (\(R_L = 1\)), favorable (0 < \(R_L < 1\)) or irreversible (\(R_L = 0\)) [24].

Table 2 shows the data for the Langmuir and Freundlich isotherms. The linear plot of \(C_e/q_e\) versus \(C_e\) in Figure 4 gave the slope of \(1/Q_0\) and intercept of \(1/(Q_0 K_L)\). The values for the coefficient correlation, \(R^2\), adsorption capacity, \(Q_0\), and energy of adsorption, \(K_L\) can be calculated from the linear plot in Figure 4 and were recorded in Table 2. The value for \(R^2\) obtained from the graph was 0.153, less than that of Freundlich isotherm and indicating less favorable adsorption of atrazine onto GAC using the Langmuir isotherm. The value of \(Q_0\) was 58.824 mg/g and indicating not a very strong monolayer adsorption to the surface. The value for \(K_L\) was 0.85 L/mg and indicating less favorable sorption energy.

The Freundlich constants are related to the sorption capacity, \(K_F\) and intensity, \(n\). These constants can be calculated from the linear plot in Figure 5 and were recorded in Table 2. The linear plot of \(\log q_e\) versus \(\log C_e\) in Figure 5 gave the slope of \(1/n\) and intercept of \(\log K_F\). The high value for \(K_F\) obtained from the graph was 33.266 L/mg and indicating favorable adsorption conditions for atrazine in aqueous solution. The value for \(R^2\) obtained from the graph was 0.749, higher than that of Langmuir isotherm and indicating favorable adsorption of atrazine onto GAC using the Freundlich isotherm.
Table 2: Langmuir and Freundlich isotherm parameter constants for adsorption of atrazine using GAC at 30 °C

<table>
<thead>
<tr>
<th></th>
<th>Langmuir Isotherm</th>
<th>Freundlich Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q₀ (mg/g)</td>
<td>Kₐ (L/mg)</td>
<td>R²</td>
</tr>
<tr>
<td></td>
<td>58.824</td>
<td>0.850</td>
</tr>
</tbody>
</table>

Figure 4: Langmuir isotherm for adsorption of atrazine using GAC at 30 °C

Figure 5: Freundlich isotherm for adsorption of atrazine using GAC at 30 °C

IV. CONCLUSION

This study showed that the GAC synthesized from oil palm shell was able to remove atrazine from water. The GAC achieved more than 95% atrazine removal in all the batch experiments. In the adsorption kinetics study, GAC synthesized from oil palm shells showed the adsorption of atrazine was of the pseudo-first-order which implies physisorption. In the adsorption isotherm study, the adsorption of atrazine was better described by the Freundlich isotherm, indicating multilayer adsorption on the heterogeneous surface of the adsorbent. The atrazine adsorption capacity of GAC was 15.132 mg/g.

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REFERENCES


