Batch Study for Pesticide Glyphosate Adsorption onto Palm Oil Fronds Activated Carbon†

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The adsorption of glyphosate from aqueous solution onto activated carbon derived from palm oil fronds (PFAC) was investigated through batch study. The effects of both initial concentration and pH of the glyphosat over the range of 25 to 250 mg/L and 2 to 12, respectively on the adsorption of the prepared PFAC were studied in batch experiments. Equilibrium data were fitted to the Langmuir, the Freundlich and the Temkin isotherm models. The results obtained from application of these models show that the best fits were achieved with the Langmuir model and a maximum monolayer adsorption capacity of 104.2 mg/g was obtained at 30 ºC. The regeneration efficiency of spent activated carbon was studied and it was found to be 94.0-96.1 %. The results indicated that PFAC has good capability as adsorbent for the removal of glyphosate from aqueous solutions.

Key Words: Glyphosate, Adsorption, Desorption, Activated carbon, Palm oil fronds.

INTRODUCTION

Pesticides are chemicals, which are commonly used in agriculture to protect crops from pest organisms including insects, plants, fungi, rodents and nematodes. They may appear as pollutants in water sources and threat to human health because of their toxicity, carcinogenicity and mutagenicity. In developed countries, drinking water quality has strict regulations regarding pesticides[1].

Presently, on a worldwide basis, intoxications attributed to pesticides have been estimated to be as high as 3 million cases of acute and severe poisoning annually, with many unreported cases and with some 220000 deaths[2]. This situation calls for urgent attention with acceptable solution for the removal of pesticides from water sources. This is because pesticides will continue to be used effectively for pest controls and the responsibility rest on us to find ways of avoiding many of the pesticides poisonings and contaminations that exist today.

Glyphosate is a newly emerging herbicide used for selective control of broadleaf weeds and sedges in beans, rice, corn, peanuts and mint. It is one of the most commonly used herbicides in agriculture and gardening. However, through leaching or run-off from agricultural lands, deposition from aerial applications and indiscriminate discharge of industrial wastewaters, glyphosate has become a reckoned source of contaminant to water resources with its attendant threats to the ecosystem and environment in general[3].

There are several methods either independent or in conjunction that have been used for the removal of pesticides from water, such as chemical oxidation with ozone[4], photo-catalytic method[5], combined ozone and UV irradiation[6], ozonation[7], membrane filtration[8] and adsorption[9]. Adsorption is one of the most frequently applied methods because of its efficiency, capacity and applicability on a large scale. The most commonly used adsorbent in adsorption processes is activated carbon due to its efficiency and economic feasibility. Utilization of activated carbon can be in the form of powder, granular and fiber or cloth. Recently, growing research interest in the production of carbon-based activated carbon has been focused on agricultural by-products. Low cost adsorbents derived from agricultural wastes have demonstrated outstanding capabilities for the removal of pollutants from wastewater. Therefore, low cost agricultural waste adsorbents can be viable alternatives to activated carbon for the treatment of contaminated wastewater. The use of cheap and eco-friendly adsorbents have been studied as an alternative substitution to activated carbon for the removal of dyes from wastewater[10].

EXPERIMENTAL

Glyphosate: Glyphosate supplied by Sigma-Aldrich Sdn Bhd, was used as the adsorbate in this study. Deionized water was used to prepare all the solutions.

Preparation and characterization of activated carbon: Palm oil fronds used as a starting material for preparation of activated carbon, which was cut into pieces, dried in air until the weight was constant. The dried pieces was then crushed using a grinder and thereafter screened to particle size range of 1-4 mm. The screened palm oil fronds were then carbonized in a stainless steel, vertical tubular reactor, placed in a tube furnace. The temperature of the furnace was ramped from room temperature to 700 ºC at heating rate of 10 ºC/min and held for 2 h under nitrogen (99.995 %) flowing at the rate of 150 cm^3/min. The char produced from the carbonization process was subsequently impregnated with KOH pellets (KOH/Char = 2.75 by weight). The impregnated char was thermally treated under nitrogen to a final temperature of 850 ºC. Once the final temperature was reached, the nitrogen gas flow was switched over to CO_2 and held under that condition for 1 h. The PFAC produced was then cooled to room temperature under nitrogen flow (150 cm^3/min) and thereafter washed with 0.1 M HCl and hot distilled water to bring the pH of the washing filtrate to about[7].

The surface area, pore size distribution and the pore volume of the developed PFAC were analyzed using Micromeritics (Model ASAP 2020, USA-surface area and porosity analyzer) employing nitrogen adsorption isotherm at 77 K. In order to determine the surface morphology of the PFAC, the sample was examined using scanning electron microscope-model: Leo Supra 35 VP Field Emission SEM.

Batch equilibrium studies:

Effect of glyphosate initial concentration and solution pH: In order to study the effect of glyphosate initial concentration and contact time on the adsorption uptake, 200 mL of glyphosate solutions with initial concentrations of 25-250 mg/L were prepared in a series of 250 mL Erlenmeyer flasks and 0.30 g of the PFAC was added into each flask covered with glass stopper. The flasks were then placed in an isothermal water-bath shaker at 30 ºC, with agitation speed of 120 rpm. At specific time intervals, samples were withdrawn for analysis, using a double beam UV-VIS spectrophotometer (Shimadzu UV-1700, Japan) until equilibrium point was reached. The effect of solution pH on the glyphosate adsorption on PFAC was also examined by varying the initial pH of the solutions between 2 and 12 (using 0.1 M HCl and/or 0.1 M NaOH as buffer solutions).

Equilibrium data fitting: Three isotherm models were used to test fit the experimental data, the Langmuir isotherm[11] the Freundlich isotherm[12] and the Temkin isotherm[13]. The linear form of the Langmuir model is:

$$C_e/q_e = C_e/q_m + 1/K_aq_m \qquad (1)$$

where, C_e is the equilibrium concentration (mg/L); q_e the amount glyphosate adsorbed at equilibrium (mg/g); q_m the adsorption for complete monolayer (mg/g); K_a is the sorption equilibrium constant (L/mg).

The linear form of Freundlich isotherm is:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \qquad (2)$$

The constants K_F and $1/n$ of the Freundlich model are the constants indicative of the relative adsorption capacity of the adsorbent and the intensity of the adsorption, respectively.

Temkin isotherm has been used in the form as follows:

$$q_e = B \ln A + B \ln C_e \qquad (3)$$

where, $B = RT/b$, b is the Temkin constant related to heat of sorption (J/mol); A is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol K) and T the absolute temperature (K).

Regeneration of activated carbon: The feasibility of regenerating the spent activated carbon was evaluated using ethanol desorption technique. Batch equilibrium tests were performed on the fresh activated carbon prepared, where 100 mL of glyphosate solution with initial concentration of 200 mg/L were placed in a 250 mL Erlenmeyer flasks. 0.30 g of the fresh PFAC was added into the flask and placed in an isothermal water bath shaker at 30 ºC, with agitation speed of 120 rpm, for 48 h until complete equilibrium was attained. The spent activated carbon was then separated from the solution and dried at 105 ºC in an oven. It was thereafter mixed with 100 mL of 95 vol. % ethanol in an Erlenmeyer flask for the desorption of the adsorbed glyphosate. The flask was kept in the isothermal water-bath shaker at the same temperature for the same time duration as the adsorption tests. Desorption percentage was calculated from equation 4:

$$\text{Desorption \%} = (C_{de} / C_{ad}) \times 100 \qquad (4)$$

RESULTS AND DISCUSSION

Effect of initial concentration and agitation time on glyphosate adsorption: The effect of glyphosate initial concentration and agitation time on the glyphosate adsorption onto the PFAC is shown in Fig. 1. It is clear that the amount of glyphosate adsorbed, q_t increased onto PFAC surface. The adsorption uptake at equilibrium was found to increase with an increase in the initial insecticide concentration as appear in Fig. 1, which shows that longer contact times were required to reach equilibrium by the glyphosate solutions of higher initial concentrations.

Fig. 1 shows that longer contact times are required by the glyphosate solutions of higher initial concentrations to reach equilibrium. The contact times needed for glyphosate solutions with initial concentrations of 25-150 mg/L to reach equilibrium onto PFAC was around 4 h. However, for higher initial concentrations (200-250 mg/L) of glyphosate solutions and required 10 h for equilibrium.
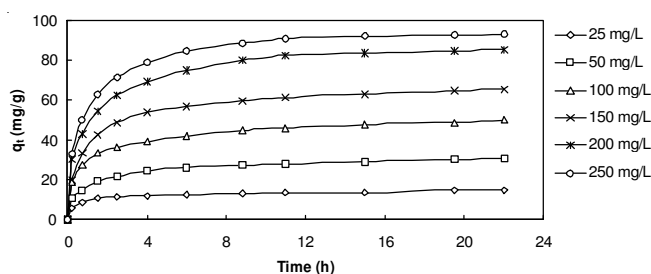

Fig. 1. Effect of glyphosate initial concentration and agitation time on adsorption capacity

Adsorption of glyphosate was fast due to the high affinity of the interacting groups on the surface of the activated carbon. The high adsorption rate at the beginning of adsorption was due to the adsorption of glyphosate to the exterior surface of

the adsorbent. The high adsorption uptake of activated carbons prepared in this work were due to the presence of functional groups such as hydroxyl, carbonyl which dissociate and hence the electrostatic attraction between the activated carbon surface and herbicide. Similar trend has been reported for glyphosate adsorption onto carbon slurry[14]. The rate of uptake is rapid in the beginning and the rate of adsorption was found to depend on the initial concentration of pesticide.

Effect of solution pH on glyphosate adsorption: The effect of pH on glyphosate adsorption was studied by varying the pH from 2 to 12 using 200 mL of a 100 mg/L fixed initial concentration of glyphosate at 30 ℃. The equilibrium adsorption of glyphosate was found to decrease slightly when the initial pH of the aqueous solution was increased from 2 to 12 (Figure not shown).

The glyphosate adsorption was significantly changed over the pH value of 2-12 as observed on the activated carbon used. The equilibrium adsorption (q_e) was found to decrease with increasing pH (Figure not shown). The observed change in solution pH could have had effect on the properties of pesticide molecules and consequently on their adsorption. Additionally, the surface functional groups of the adsorbent make the adsorption process complicated. It is also possible that the surface properties of the activated carbon have been altered as a result of the pH of the solution. Thus, the surface charge would depend on the solution pH and the surface characteristics of the carbon[15].

Adsorption isotherm: The equilibrium data for glyphosate adsorption on PFAC were modeled with three linearized expressions of the Langmuir, the Freundlich and the Temkin isotherm models (Figures not shown). Table-1 summarizes all the constants and correlation coefficients, R^2 of these three isotherm models at 30 ℃. The Langmuir model yielded the best fit with R^2 which were higher than 0.962. The monolayer adsorption capacity according to Langmuir model was 104.2 mg/g.

Regeneration of activated carbon: (PFAC) that adsorbed herbicide was regenerated by ethanol. The desorption of glyphosate from spent PFAC was repeated for four cycles for adsorption and four cycles for desorption using the same activated carbon for the starting cycle. The regeneration efficiency was found to be 94-96.1 %. This result indicates that the prepared activated carbon has a good regeneration and reusability characteristics for the adsorption of glyphosate and can be used as an alternative to the presently available commercial activated carbons.

Conclusion

This work examined the feasibility of activated carbon prepared from palm oil fronds for the adsorption of herbicide from aqueous solutions over a wide range of concentrations. It was found that the PFAC was very effective for this purpose. Equilibrium data were fitted to the Langmuir, Freundlich and Temkin isotherms and the equilibrium data were best described by the Langmuir isotherm model, with the maximum monolayer adsorption capacity of 104.2 mg/g. Ethanol desorption technique was efficient in regenerating the spent activated carbon and this provides a good ground for the reusability of the PFAC in subsequent adsorption runs.

TABLE-1
LANGMUIR, FREUNDLICH AND TEMKIN ISOTHERM
MODEL PARAMETERS AND CORRELATION COEFFICIENTS
FOR ADSORPTION OF GLYPHOSATE ON PFAC AT 30 ℃

Isotherm models	Parameters		
Langmuir	q_m (mg/g)	b (L/mg)	R^2
	104.2	0.054	0.962
Freundlich	K_F (mg/g(L/mg)$^{1/n}$)	1/n	R^2
	12.81	0.427	0.941
Temkin	A (L/g)	B	R^2
	1.17	19.11	0.943

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