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Batch study for herbicide bentazon adsorption onto branches of pomegranates trees activated carbon

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ABSTRACT

The adsorption of herbicide bentazon from aqueous solution onto branches of pomegranates trees activated carbon (BPTAC) was investigated through batch study. The effects of both initial concentration and pH of the bentazon over the range of 25–250 mg/L and 2–12, respectively, on the adsorption of the prepared BPTAC 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 80 mg/g was obtained at 30˚C. The regeneration efficiency of spent activated carbon was studied and it was found to be 92–96%. The results indicated that BPTAC has good capability as adsorbent for the removal of bentazon from aqueous solutions.

Keywords: Branches of pomegranate trees activated carbon; Bentazon; Adsorption

1. Introduction

The challenges of the ever increasing world population on agricultural sector to meet the consequent increase in basic necessities of life have significantly altered the traditional eco-friendly agricultural practices. A pesticide is any substance used to control pests. Pests may be target insects, vegetation, fungi, etc. Most control the pests by poisoning them. Unfortunately, pesticides can be poisonous to humans as well. Some are very poisonous, or toxic and may seriously injure or even kill humans [1]. The herbicide bentazon 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, bentazon is becoming a reckoned source of contaminant to water resources with its attendant threats to ecology and environment in general [2].

Adsorption has been widely used to remove toxic compounds from polluted waters; this technology is presently the most viable option being employed for the removal of such pesticides from wastewaters [3]. Activated carbon or other highly porous materials, such as synthetic resins, are commonly utilized.

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Activated carbon is a widely used adsorbent in the treatment of wastewater and drinking water. This is because activated carbon possessed desirable physio-chemical properties (good mechanical strength, chemical stability in diverse media, and commendable pore sizes distribution in addition to its extensive specific surface area) indispensable for such operations [4]. However, commercially available activated carbons are generally expensive. Hence, special emphasis is currently placed on the preparation of activated carbons from agricultural by-products due to the growing interest in low-cost activated carbons and preferably from renewable sources [5]. Therefore, in recent years, this has prompted a growing research interest in the production of activated carbons from renewable and cheaper precursors which are mainly industrial and agricultural by-products; therefore, the objective of this work was to study the adsorption of an herbicide bentazon onto activated carbon prepared from branches of pomegranates trees.

2. Methods

2.1. Bentazon

Bentazon (99.99% purity) obtained from Sigma–Aldrich (M) Sdn Bhd, Malaysia, was used as adsorbate. Distilled water was used to prepare all solutions.

2.2. Preparation and characterization of activated carbon

BPT obtained from the pomegranate orchards located within the Baghdad city, was cut into pieces and dried in air until the weight was constant. The dried sample was then crushed using a grinder and thereafter screened to particle size range of 1–3 mm. The screened BPT were then carbonized in a stainless steel, vertical tubular reactor, and placed in a tube furnace. The temperature of the furnace was ramped from room temperature to 600°C at heating rate of 10°C/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 = 1.5 by weight). The impregnated char was thermally treated under nitrogen to a final temperature of 750°C. 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 branches of pomegranates trees activated carbon (BPTAC) 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 sample was examined using scanning electron microscope (SEM)—model: Leo Supra 35 VP Field Emission SEM.

2.3. Batch equilibrium studies

2.3.1. Effect of bentazon initial concentration and pH solution

In order to study the effect of bentazon initial concentration and contact time on the adsorption uptake, 200 mL of bentazon solutions with initial concentrations of 25–250 mg/L were prepared in a series of 250-mL Erlenmeyer flasks, and 0.20 g of the BPTAC was added into each flask covered with glass stopper. The flasks were then placed in an isothermal water-bath shaker at 30°C, 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) at 232 nm, until equilibrium point was reached. The effect of solution pH on the bentazon adsorption on BPTAC 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). In a typical run, the bentazon initial concentration was fixed at 100 mg/L, with activated carbon dosage of 0.20 g/200 mL and solution temperature of 30°C.

2.3.2. Equilibrium data fitting

Three isotherm models were used to test fit the experimental data, the Langmuir isotherm [6] the Freundlich isotherm [7] and the Timken isotherm [8]. The linear form of the Langmuir model is:

$$C_e/q_e = C_e/q_m + 1/K_a q_m \quad (1)$$

where C_e is the equilibrium concentration (mg/L); q_e the amount bentazon 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:

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

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.

The Timken isotherm has been used in the form as follows:

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

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).

2.3.3. Regeneration of activated carbon

The feasibility of regenerating the spent activated carbon was evaluated using ethanol desorption technique [9]. Batch equilibrium tests were performed on the fresh activated carbon prepared, where 100 mL bentazon solution with initial concentration of 200 mg/L were placed in a 250-mL Erlenmeyer flasks. About 0.20 g of the fresh BPTAC was added into the flask and placed in an isothermal water bath shaker at 30˚C, 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˚C in an oven. It was thereafter mixed with 100 mL of 95 vol. % ethanol in an Erlenmeyer flask for the desorption of the adsorbed bentazon. 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 Eq. (4):

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

3. Results and discussion

3.1. SEM characteristics of BPTAC

Fig. 1 shows the SEM image of the produced BPTAC. The BPTAC depicts a surface containing a well-developed pores expected of a good absorbent, in which the carbonaceous matters and salts that could have blocked the pores as seen in the precursor had been leached off by the activation process, showing the efficacy of the thermo-chemical activation method adopted in this investigation.

Fig. 1. SEM image of the BPTAC (magnification: 1,000×).

3.2. Effect of initial concentration and agitation time on bentazon adsorption

The effect of initial concentration and agitation time on the bentazon adsorption onto the BPTAC is shown in Fig. 2. It is clear that the amount of bentazon adsorbed, q_t increased onto BPTAC surface. The adsorption uptake at equilibrium was found to increase with an increase in the initial herbicide concentration as appear in Fig. 2, which shows that longer contact times were required to reach equilibrium by the bentazon solutions of higher initial concentrations.

The contact time needed for bentazon solutions with initial concentration of 25–150 mg/L to reach equilibrium on BPTAC was around 2–4 h; at the mean time the contact times for higher initial concentrations (200–250 mg/L) equilibrium times of 8–10 h were required.

Adsorption of bentazon 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 bentazon 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. The rate of uptake is rapid in the beginning and the rate of adsorption was found to depend on the initial concentration of pesticide.

3.3. Effect of solution pH on bentazon adsorption

The effect of the pH of solution on bentazon adsorption was studied by varying the pH from 2 to

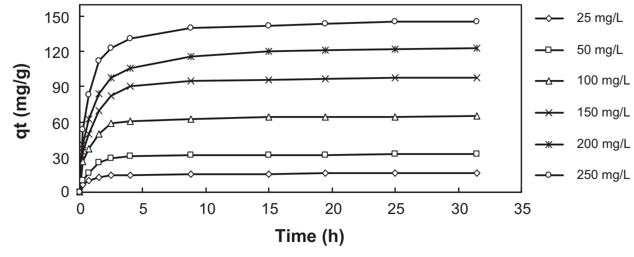

Fig. 2. Effect of initial concentration and agitation time on bentazon adsorption capacity.

Table 1
Langmuir, Freundlich, and Temkin isotherm model parameters and correlation coefficients for adsorption of bentazon on BPTAC at 30˚C

Isotherm models	Parameters		
Langmuir	q_m (mg/g)	b (L/mg)	R^2
	80	0.061	0.97
Freundlich	K_F (mg/g(L/mg)$^{1/n}$)	$1/n$	R^2
	12.48	0.405	0.960
Temkin	A (L/g)	B	R^2
	1.18	13.75	0.890

12 using 200 mL of a 100 mg/L fixed initial concentration of bentazon at 30˚C. The equilibrium adsorption of bentazon was found to decrease slightly when the initial pH of the aqueous solution was increased from 2 to 12 (figure not shown). This may be due to the presence of excess H^+ ions which accelerates the removal of the bentazon with the anion OH^- in the aqueous solution. 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 [10].

3.4. Adsorption isotherm

The equilibrium data for bentazon adsorption on BPTAC 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˚C. The Langmuir model yielded the best fit with R^2 which were higher than 0.993.The monolayer adsorption capacity according to Langmuir model was 80 mg/g.

3.5. Regeneration of activated carbon

BPTAC that adsorbed bentazon was regenerated by ethanol. The desorption of bentazon from spent BPTAC 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 92–96%. This result indicates that the prepared activated carbon has a good regeneration and reusability characteristics for the adsorption of bentazon and can be used as an alternative to the presently available commercial activated carbons.

4. Conclusion

This work examined the feasibility of activated carbon prepared from BPT for the adsorption of bentazon herbicide from aqueous solutions over a wide range of concentrations. It was found that the BPTAC 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 80 mg/g. Ethanol desorption technique was efficient in regenerating the spent activated carbon and this provides a good ground for the reusability of the BPTAC in subsequent adsorption runs.

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