Adsorption of metribuzin from aqueous solutions using activated carbon prepared from olive-waste cake

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Abstract The aim of the present work is the valorization of activated carbon prepared from industrial solid waste in the adsorption of metribuzin pesticide. The present study constitutes of two principal parts. The first part includes chemical activation of raw material and structural characterization of the activated carbon. In the second part, different parameters likely to have an influence on the adsorption capacity of metribuzin such as adsorbent dosage, initial solution pH and initial Metribuzin concentration were investigated. The experimental data were analyzed by the Freundlich, Langmuir, Dubinin-Radushkevich and Temkin isotherm models. The surface area of chemically modified activated carbon was 1418 $m^2 g^{-1}$. The experimental data indicated that the adsorption isotherms are well described by the Langmuir isotherm equation and the calculated adsorption capacity was 144.93 mg g^{-1} at 318 K. The results indicated that the activated carbon prepared from olive-waste cake is very effective for the adsorption of metribuzin from aqueous solutions.

Keywords: Activated carbon, olive-waste cake, adsorption, pesticide.

1. Introduction

Metribuzin is one of the most organometallics herbicides used in Turkey as well as all over the world. Metribuzin is a synthetic organic compound. It is a selective triazinone herbicide used primarily to discourage the growth of broad leaf weeds and annual grasses among vegetable crops and turf grass (Behloul *et al*., 2016). Many processes have been proposed for metribuzin removal from water and groundwater. Electrochemical treatment, ultraviolet oxidation, electro-activated granular carbon, and membranes techniques are among the most commonly used methods; each has its merits and limitation in application (Behloul *et al*., 2016; Kitous *et al*., 2012). The adsorption is currently considered as an alternative process for pesticide pollutant elimination. The adsorption method was proven to be more sophisticated and efficient compared to other methods for pesticide removal from wastewater, due to its low-cost, easy availability, simplicity of design and ease of operation (Senthilkumar *et al*., 2006; Gerçel *et al*., 2007).

Activated carbon materials have a special place among the adsorbents, as they are known to be capable of adsorbing various organic compounds for a long time. The number of studies on adsorption of pesticides on carbon materials from aqueous solution has increased in recent years (Behloul *et al*., 2016; Ayranci and Hoda, 2004; Tang *et al*., 2015; Kitous *et al*., 2012).

The present study proposes the use of a new adsorbent, activated carbon derived from olive-waste cake for the treatment of water charged with metribuzin pesticide. The adsorption of metribuzin on activated carbon was studied with respect to adsorbent dosage, initial solution pH and initial Metribuzin concentration. The experimental data were analyzed by the Freundlich, Langmuir, Dubinin-Radushkevich and Temkin isotherms.

2. Methods

2.1. Material

Olive-waste cake was supplied by the HISAR Olive Ind. Inc. (Manisa, TURKEY). All chemical reagents used in this study were of analytical grade. Metribuzin ($C_8H_{14}N_4OS$) with high purity (≥98%) was supplied from Sigma-Aldrich.

a. Preparation and characterization of activated carbon

In this study, chemical activation of olive-waste cake was performed using zinc chloride ($ZnCl_2$) with an impregnation ($ZnCl_2$:olive-waste cake) ratio of 3:1. About 10 g of the impregnated sample was placed on a ceramic crucible in the tubular reactor (Protherm PTF 12) and heated up to the final activation temperature (800 °C) under the nitrogen flow (≈200 $cm^3 min^{-1}$) at heating rate of 5 $°C min^{-1}$ and held for 2 h at this final temperature. Proximate analyses of activated carbon were determined according to the international standards. The surface areas of olive-waste cake and activated carbon were determined by Micromeritics Instruments, Tristar II 3020 by using the nitrogen adsorption-desorption isotherms at 77 K.

b. Adsorption experiments

The studied variables were initial pH, adsorbent dosage and initial metribuzin concentration of solution. In the procedure for the batch pH studies, 0.2 g adsorbent and 100 mL of metribuzin solution containing 100 mgL^{-1}

metribuzin were mixed and shaken at 298 K for 24 h using a temperature controlled water bath with a shaker (GFL). After adsorption, samples were filtered and then the concentration of metribuzin in the supernatant solution was analyzed. All concentrations were measured by using UV spectrophotometer (Shimadzu UV-Vis 1240) at 293 nm. The initial pH values of the solutions were adjusted to different values (2; 3; 5; 7; 9,20; 11 and 12) by adding dilute NaOH or HCl solutions. The pH was measured with pH-meter (Mettler-Toledo). After adsorption, the pH value providing the maximum metribuzin removal was determined. Also, for the purpose of researched the effect of adsorbent dosage, batch experiments were carried out at 298 K and optimum pH value of the solution for 24 h shaking period by adding different amounts of activated carbon (0.1-0.8 g) into each 100 ml metribuzin solution (100 mgL^{-1}). The removal percentage of metribuzin was calculated according to the following equation:

$$Removal\ (\%) = \frac{C_0 - C_e}{C_o} x100 \quad (1)$$

Where C_0 and C_e (mgL^{-1}) are initial and equilibrium concentrations of the pesticide (metribuzin), respectively (Yang and Qui, 2010).

For the adsorption isotherm and investigation of effect of initial concentration on metribuzin removal, 0.2 g adsorbent was contacted with 100 mL metribuzin solution with different initial concentration (50, 100, 150, 200, 250 and 300 mgL^{-1}) without adjusting pH (pH value 9.20). The flasks were agitated at 120 rpm using a temperature controlled water bath with a shaker (GFL), and maintained at 318 K for 24 h until the equilibrium was reached. The suspensions were filtered and metribuzin concentrations were measured using a UV spectrophotometer. Metribuzin uptake at equilibrium, q_e (mg g^{-1}), was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (2)$$

Where C_0 and C_e (mgL^{-1}) are initial and equilibrium concentrations of the metribuzin, respectively, V (L) is the volume of the aqueous metribuzin, and w (g) is the weight of activated carbon used. The equilibrium data were then fitted using Langmuir, Freundlich, Dubinin-Radushkevick (D-R) and Temkin isotherm models (Gerçel *et al*., 2007; Mahapatra *et al*., 2012; Angın, 2014; Demiral *et al*., 2008).

The linear form of Langmuir isotherm equation;

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \quad (3)$$

$$R_L = \frac{1}{1 + K_L . C_0} \quad (4)$$

The logarithmic form of Freundlich isotherm equation;

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

Dubinin–Radushkevich isotherm equations;

$$q_e = q_s \exp(-B\varepsilon^2) \quad (6)$$

$$\varepsilon = \mathrm{RT} \ln\left[1 + \frac{1}{C_e}\right] \quad (7)$$

$$E = \frac{1}{\sqrt{2B}} \quad (8)$$

The lineer form of Temkin isotherm equation;

$$q_e = B_1 \ln \mathrm{A} + B_1 \ln C_\mathrm{e} \quad (9)$$

3. Results and discussion

3.1. Characterization of activated carbon

The activated carbon prepared from olive-waste cake contains 0.22 wt.% ash, 5.81 wt.% volatile matter and 93.97 wt% fixed carbon. The porosity has a strong effect on the adsorption properties of the activated carbon. The specific surface area and total pore volume of activated carbon were found to be 1418.0 m^2g^{-1} and 0.410 cm^3g^{-1}, respectively. The activated carbon produced from olive-waste cake in this study contained both micropores and mesopores but the mesopore volume was larger than the micropore volume.

3.2. Effect of initial pH

The initial pH of solution is one of the most important factors influencing the properties of adsorbate, adsorbent and the adsorption process. The influence of initial pH was attributed to the electrostatic interaction between the pesticide and the activated carbon surface (Tang *et al*., 2015). The effect of initial pH on the removal of metribuzin is shown in Fig. 1. As shown in Fig. 1, the removal of metribuzin was observed close together for pH value 2, 5, 7 and 9.20 (96.90 wt.%; 96.86 wt.%, 96.39 wt.% and 97.00 wt.%, respectively) and after pH 9.20, decreased in the amount of adsorbed metribuzin was observed on proceeding further till pH 12 (91.0 wt.%). The maximum removal of metribuzin was reached at the original solution pH value (9.20) with 48.50 mgg^{-1} value. Thus pH 9.20 (original value) was selected as the optimum pH value for all further experiments.

3.3. Effect of adsorbent dosage

The effect of dosage of activated carbon on the percentage removal of metribuzin is shown in Fig. 2. It is apparent that the percentage removal of metribuzin was increased by increasing the activated carbon dosage. This was the reason that the number of available adsorption sites was increased by increasing the adsorbent dosage (Wang *et al*., 2010). When the activated carbon dosage was 0.2 g/100 mL, the removal percentage of metribuzin can reach

97.00%. The results also indicate that the removal efficiency increases up to the optimum dosage (0.2 g/100 mL) beyond which the removal efficiency is negligible.

3.4. Adsorption isotherms

The effect of initial metribuzin concentration on adsorption was investigated. The amount of adsorbed metribuzin at equilibrium (q_e) increased from 24.69 to 131.78 mgg^{-1} as the initial metribuzin concentration was increased from 50 to 300 mg L^{-1}. This was due to increase in the driving force of the concentration gradient, as an increase in the initial metribuzin concentration.

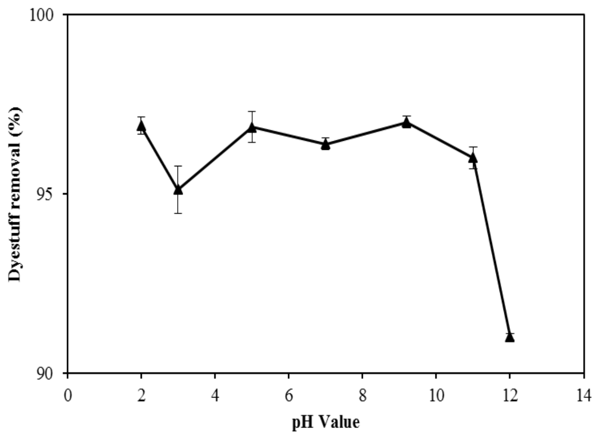

Figure 1. Effect of solution pH on the adsorption of metribuzin onto activated carbon.

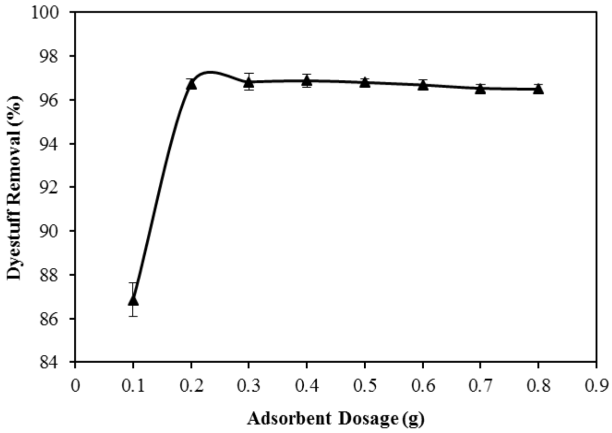

Figure 2. Effect of adsorbent dosage on the adsorption of metribuzin onto activated carbon.

The adsorption isotherm describes how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state (Yang and Qui, 2010). The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose (Lin *et al*., 2013; Li *et al*., 2013). In this study, four isotherms models were used for describing the results, namely the Langmuir, Freundlich, Dubinin–Radushkevich (D-R) and Temkin isotherm. Comparison of isotherm models for metribuzin adsorption onto activated carbon are shown in Fig. 3. Also, the fitting results, i.e. isotherm constants and correlation coefficients are shown in Table 1.

For Langmuir adsorption isotherm, one of the essential characteristics could be expressed by dimensionless constant (R_L) called equilibrium parameter. The value of R_L indicates the type of isotherm to be irreversible (R_L=0), favourable (0<R_L<1), linear (R_L=1) or unfavourable (R_L>1) (Yang and Qui, 2010; Mahapatra *et al*., 2012). By processing the above equation, R_L value for investigated pesticide-adsorbent system was found to be between 0.013-0.074 and confirmed the activated carbon is favourable for adsorption of metribuzin under conditions used in this study. The Langmuir isotherm parameters, Q_0 and K_L, was found 144.93 mg g^{-1} and 0.251 L mg^{-1}, respectively.

Table 1. Adsorption isotherm constants for adsorption of metribuzin onto activated carbon at 318 K.

Isotherms	Constants			
Langmuir	Q_o *(mg g^{-1})*	K_L *(L mg^{-1})*	R_L	R^2
	144.93	0.251	0.013-0.074	0.9955
Freundlich		*K (mg g^{-1}).(L mg^{-1})$^{1/n}$*	*n*	R^2
		34.83	2.38	0.9582
Dubinin-Radushkevich	q_s *(mg g^{-1})*	*B (mol^2 kj^{-2})*	*E (kj mol^{-1})*	R^2
	96.59	0.30	1.291	0.8280
Temkin		*A(L g^{-1})*	*B*	R^2
		3.485	27.709	0.9786

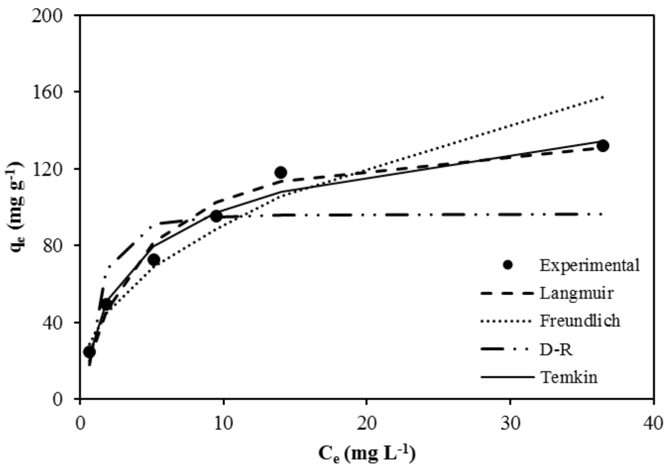

Figure 3. Comparison of different isotherm models for the adsorption of metribuzin onto activated carbon.

The can also be concluded from the Freundlich model fitting results. Magnitude of the exponent, 1/n, gives an indication of the favourability of adsorption (Yang and Qui, 2010; Mahapatra *et al*., 2012). Values of 1/n were found to be <1 in this study (Table 1). K_F is a rough indicator of the adsorption capacity. In general, as the K_F value increases, the adsorption capacity of the adsorbent for a given adsorbate increases. A high value of K_F is indicative of a high adsorption capacity (Behloul *et al*., 2016; Kitous *et al*., 2012).

The Dubinin–Radushkevich model used to determine the characteristic porosity and the apparent free energy of adsorption (Ada *et al*., 2009). The experimental data were fitted well by Dubinin–Radushkevich isotherm model. The magnitude of *E* is useful for estimating the type of adsorption process. The magnitude of *E* is 8-16 kJmol^{-1}, adsorption type can be explained by chemical adsorption. It's accepted that when the adsorption energy is below 8 kJ mol^{-1}, the type of adsorption can be defined as physical adsorption (Senthil Kumar *et al*., 2010; Demiral *et al*., 2008). According to the calculated mean free energy (1.291 kJmol^{-1}), the type of adsorption of metribuzin on the activated carbon was described as physical adsorption.

The Temkin isotherm model predicts a uniform distribution of binding energies over the population of surface binding adsorption sites. The range and distribution of the binding energies should depend strongly on the density and distribution of functional groups both on the pesticide (metribuzin) and adsorbent surfaces. The Temkin adsorption isotherm model was chosen to determine the adsorption potentials of the adsorbent for adsorbates (Demiral *et al*., 2008; Wang *et al*., 2010; Ada *et al*., 2009). The Temkin adsorption potentials was 3.485 L g^{-1} at 318 K.

The Langmuir model fitted the experimental data better than other isotherm models, indicating the adsorption of metribuzin onto the activated carbon tended to monolayer adsorption. Furthermore, the R^2 values of the four isotherm models descend in the order of: Langmuir > D-R > Temkin > Freundlich.

4. Conclusion

This study demonstrated the feasibility of olive-waste cake as a promising precursor for the production of activated carbon with a noticeable adsorption capacity for the removal of metribuzin. The optimum adsorbent dosage can be used as 0.2 g/100 mL because of the metribuzin removal efficiency is negligible value at different adsorbent dosage. The batch adsorption studies clearly suggest that the high adsorption capacity (144.93 mg g^{-1}) of activated carbon in neutral solutions (pH around 9.20) is due to the strong electrostatic interactions between its adsorption site and pesticide (metribuzin). The Langmuir isotherm model, which describes monolayer physical adsorption, was found to be consistent with experimental data and this results supported by the Dubinin-Radushkevich isotherm model. The results showed that the activated carbon from olive-waste cake can be effectively applied for the removal of pesticides from wastewater.

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