

Competitive and non-competitive adsorption of atrazine and diuron on alluvial soil

Mohamed R. Fouad¹ and Ahmed F. El-Aswad¹

ABSTRACT

The competitive and non-competitive adsorption of herbicides atrazine and diuron individual and in binary combination on alluvial soil depends upon the batch equilibration technique were evaluated. The results indicated that the optimum wavelengths obtained from spectral curves were 222 nm and 289 nm and the k values obtained from calibration curves were 0.1327 and 0.0061 for atrazine and diuron, respectively. The equilibrium time for atrazine and diuron in clay loam soil is 3 hours. The adsorption of atrazine and diuron individually in clay loam soil is fitted with Freundlich model. The isotherms of either atrazine and diuron alone or in the binary mixture are S-type. The adsorption capacity of tested clay loam soil is more for atrazine neither individual nor in binary combination than that for diuron individual and in binary combination. The adsorption capacity of tested clay loam soil is lower for individual atrazine compared to that in binary combination with diuron. While, the adsorption capacity of tested clay loam soil is higher for individual diuron compared to that in the binary combination. In general, the relatively weak sorbing diuron in competitive system might depend on the available binding sites which influenced by atrazine. However, the sorption of the relatively stronger adsorbing atrazine was less affected by diuron at the same concentration range.

Key words: adsorption- Competitive- non-competitive- Atrazine- diuron- soil.

INTRODUCTION

Pesticides mainly reach the soil through agricultural practices. The pesticide-soil interaction is influenced by pesticide properties, soil characteristics and environmental factors (Rodríguez-Liébana *et al.*, 2011). Once the pesticides application, various physico-chemical processes were occurred. The most processes is they adsorb on the soil particles (ElShafei, 2009.) Sorption is a dynamic process in which molecules are continually distributed between the soil solution and the particle surfaces of soil (Patakioutas and Albanis, 2002). Different physical and chemical characteristics of the pesticides cause differences in their adsorption in the same soil type (Scribner *et al.*, 1992).

The information in literature is lack about the competitive sorption of herbicides on the binding sites in soil system and their potential mobility which

necessary to know the transport as well as the fate of herbicides in environment. When the sorption sites on the soil surfaces are limited, the competitive sorption takes place (Pignatello, 1991). The competitive sorption is also due to the overlapping in the set of the surface sites (Xing *et al.*, 1996). The competitive sorption could be play an important role in the fate of pesticides in agricultural soil due to the diversity of the agrochemicals (Pateiro-Moure *et al.*, 2008).

Atrazine is a selective herbicide belonging to the s-triazine family. It has been used since the 1950s as a pre- or postemergence against annual grasses and broadleaf weeds and extensively applied during 1990–1993 in the United States (Radosevich *et al.*, 1996; Vencill, 2002). It is among the most widely applied herbicides in many of countries as well as relatively high stability in soils (Capriel *et al.*, 1985; Blume *et al.*, 2004; Sanchez-Martin *et al.*, 2004) and high leaching potential (Bintein and Devillers, 1996; Steinheimer and Scoggin, 2001; Tomkins and Ilgner, 2002; Drevenkar *et al.*, 2004). Therefore, atrazine was banned in Germany in 1991 then throughout Europe in 2004. Although, the threshold limit of atrazine in ground- and drinking water of 0.1 mg L⁻¹. Frequent exceedances were recorded and it is still found at relatively a constant level in groundwater (Vonberg *et al.*, 2014).

Diuron is an herbicide belonging to the phenylurea compounds, it is used as a pre- or postemergence against grasses and broadleaf weeds. Diuron has been used for about 50 years. The European CommissionIt considered diuron a Priority Hazardous Substance (Directive, 2000/60/EC). In addition, the US-EPA has classified diuron as a 'known/likely' carcinogen since 1997 (Djebbar *et al.*, 2008). Diuron was monitored in runoff water and soil until 70 days after application (Dores *et al.*, 2009). The groundwater contamination by diuron has become a serious problem. In Dutch coastal and United Kingdom, a higher level of diuron than the permitted (0.1 µg L⁻¹) was detected (Lamoree *et al.*, 2002; UK-EPA, 2002).

This work presents an attempt to detect the potential of competitive and non-competitive adsorption of atrazine and diuron in clay loam soil that could be occurred in the agricultural environment by applying of batch equilibration adsorption experiments.

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MATERIALS AND METHODS

Tested herbicides:

Atrazine (6-chloro-4-N-ethyl-2-N-propan-2-yl-1,3,5-triazine-2,4-diamine). Technical grade (98%), it was supplied from the Central Laboratory of Pesticides, Giza, Egypt. Atrazine has high to slight mobility in soil.

Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea]. Technical grade (99%), it was supplied from the Central Laboratory of Pesticides, Giza, Egypt. Diuron has moderate to low mobility in soil and the water solubility is 42.0 mg/L. It's persistent is high.

Tested soil:

The soil used in this study is a common type of the Egyptian soil (alluvial soil) sampled from the surface layer (0-20 cm) from different locations have no history of atrazine and diuron treatments at the Research Farm, Agriculture College, Abis, Alexandria. The air-dry soil samples were sieved at 2 mm and analyzed according to the Standard Methods. In general, the physicochemical properties of tested soil were as follows: pH = 7.78; EC = 1.73 ds m⁻¹; total carbonate = 7.8%; OC = 0.54% and clay loam texture of 24.1% clay, 12.1% silt and 63.8% sand.

Measurements of tested herbicides:

The concentrations of atrazine and diuron were measured by a UV-Vis Spectrophotometer (Thermo Corporation, Nicolet, evolution 100). To determine the optimum wavelength (λ_{max}) that is specific for atrazine and for diuron, a scanning range of 200–400 nm was used to obtain a spectral density curve (S-D curve) of each tested compound. A standard calibration curve (C-D curve) of each herbicide was created by plotting triplicates (n = 3) of known atrazine and diuron concentrations equivalent to 0.1–100 mg/mL against its corresponding absorbance at the optimum obtained λ_{max} . The obtained k value as the slope of the standard curve was used to calculate the herbicide concentration. For quality assurance and control, triplicate samples including controls and blanks were used.

Adsorption experiments

Adsorption kinetic:

The equilibrium time of the atrazine and diuron adsorption was determined at different shaking intervals; 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, 6.0, 12.0 and 24.0 hours.

Adsorption isotherm:

The competitive and non-competitive adsorption of atrazine and diuron at room temperature was determined in a batch-equilibrium system according to OECD guideline 106 (Long, 2000). Soil samples of 1g were weighed into bottles (50-mL glass) for atrazine and/or

diuron and adjusted with 0.01 M CaCl₂ to reach the appropriate soil-solution ratio (1:10). The stock solutions equivalent to 50 mgL⁻¹ of atrazine or diuron were prepared in methanol then mixing with 0.01 M CaCl₂ solution. The adsorption was measured according to the procedure previously reported (El-Nahhal and Lagaly, 2005). The herbicides were added to reach concentrations equivalent to 5, 10, 20, 30, 40 and 50 $\mu\text{g g}^{-1}$ dry weight soil for atrazine and/or diuron. The samples were shaken for 3 h (25°C, 150 revolutions min⁻¹) Then, the samples were centrifuged (3000 rpm) for 5 min. After that, the concentration of atrazine or diuron in the supernatant was determined by UV-Spectrophotometer. Depends upon the difference in herbicide concentration between the initial and final equilibrium solutions, the amount of herbicide retained by the adsorbent was calculated. Sorption isotherms were fitted to the logarithmic form of the Freundlich equation: $\log C_s = \log K_f + \frac{1}{n} \log C_e$ where C_s ($\mu\text{mol kg}^{-1}$) is the amount of the herbicide sorbed at the equilibrium concentration, C_e ($\mu\text{mol L}^{-1}$), and K_f and $\frac{1}{n}$ are constants that characterize the relative sorption capacity and the sorption intensity, respectively, for the herbicides. Regarding to binary mixture adsorption, each single concentration mentioned above of atrazine and diuron was collected and mixed together to form a concentration of the mixture of atrazine + diuron. Then concentrations were mixed in soil and used for competitive adsorption test.

RESULTS AND DISCUSSION

Spectral curve (SD-curve):

The scanning of atrazine and diuron solutions (equivalent to 5 ppm) at 200 to 400 nm showed that the λ_{max} values obtained equal 222 and 289 nm, respectively (Fig. 1). The same value of λ_{max} was obtained for atrazine (Comber, 1999). However, it was found that the diuron λ_{max} equals 251 nm (Paterlini and Nogueira, 2005).

Calibration curve (CD-curve):

Different concentrations of atrazine in range of (1-10 $\mu\text{mol/L}$) and diuron (10-200 $\mu\text{mol/L}$) were measured at the appropriate λ_{max} . The k values were obtained from the curves as a slope, 0.1327 for atrazine and 0.0061 for diuron (Fig. 2).

Adsorption kinetic:

To determine contact time required for adsorption equilibrium attained, preliminary adsorption experiments of atrazine and diuron were conducted. The adsorption kinetics exhibited two distinct stages, rapid adsorption within 3 h followed by slow adsorption. This phenomenon was due to a large number of vacant

surface sites were available for adsorption within the first 3h. Also the equilibrium time was about 2.5 h in other study (Liu *et al.*, 2010).

Non-competitive adsorption of tested herbicides:

The equilibration procedure of the tested herbicides and soil was the same as described for the kinetics experiment. Different volumes of stock atrazine or diuron solutions were added to obtain different initial concentrations of tested herbicides with constant soil-liquid ratio of (1:10). The adsorption isotherms of atrazine and diuron were determined at 20 °C. Both compounds atrazine and diuron generally show S-type isotherms (Fig. 3A and B). Accordingly, the compound-

solvent interaction would predominate in the soil which prevents the adsorption at low concentration (Limousin *et al.*, 2007). Therefore, the quantity adsorbed of both herbicides greatly increase with slight increase of the equilibrium concentration, providing almost vertical shape curve particularly in the case of atrazine. It suggests a high affinity between the solute molecules and solid surface. To describe the adsorption of tested herbicides the Freundlich equation has been employed. The isotherms fitted Freundlich model were showed in Fig. (4 A and B). The fitting of Freundlich equation with the adsorption data was shown in Table 1.

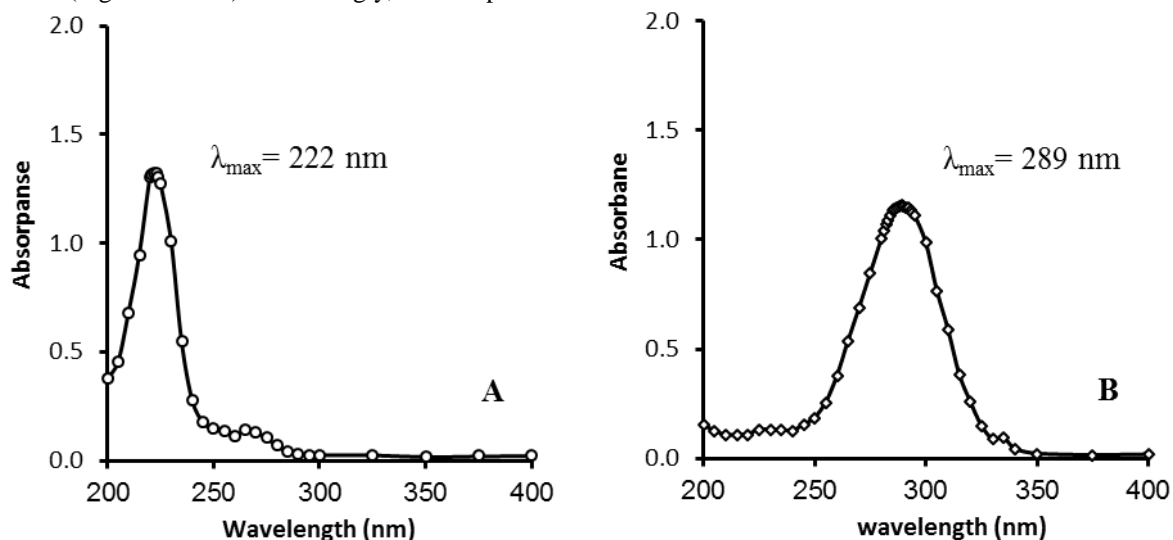


Fig. 1. Spectral-Density (S-D) curves of atrazine (A) and diuron (B). 200 to 400 nm spectra are plotted and clearly show the maximum wavelength is 222 nm for atrazine and 289 nm for diuron by UV-Spectrophotometric method

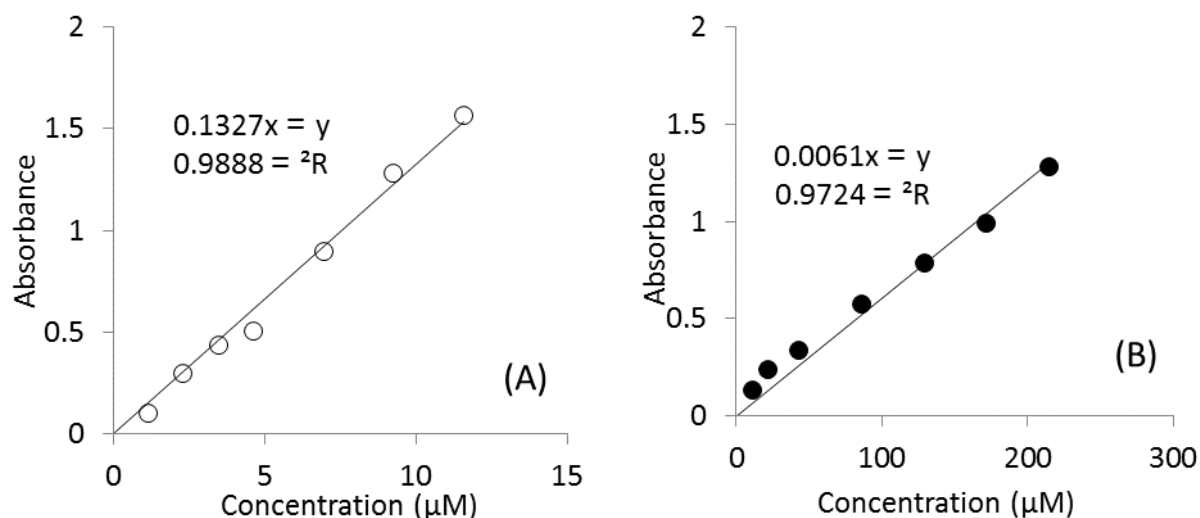


Fig. 2. Calibration-Density (C-D) curves of atrazine (A) and diuron (B). The slope as a k value is 0.1327 for atrazine and 0.0061 for diuron by UV-Spectrophotometric method

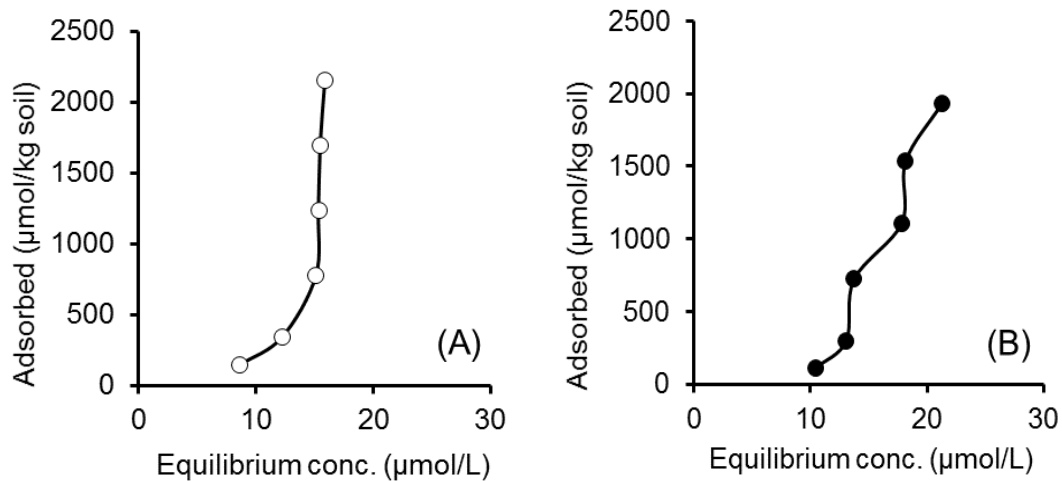


Fig. 3. Non-competitive adsorption isotherms of atrazine (A) and diuron (B) on clay loam soil

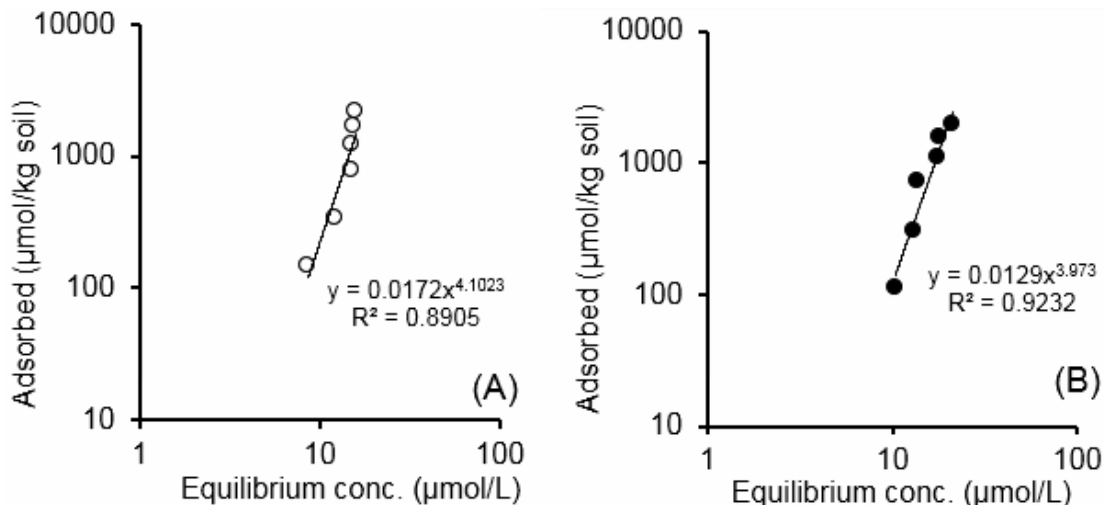


Fig. 4. Non-competitive adsorption isotherms of atrazine (A) and diuron (B) on clay loam soil fitted in Freundlich model

The determination coefficients (R^2) were 0.891 and 0.923 for atrazine and diuron, respectively. The description of the adsorption by Freundlich equation is high accurate, thus it is used in widespread to describe the adsorption on heterogeneous surfaces such as the soil particles (Stumm and Morgan, 1981). Examination of the K_f parameters shows that for atrazine 0.017, whereas for diuron its value was 0.013. The $1/n$ values were >1 for the tested herbicides (which is typical of S-type isotherm).

Table 1. Freundlich non-competitive adsorption parameters of atrazine and diuron

Compounds	K_f	$1/n$	R^2
Atrazine alone	0.017	4.102	0.891
Diuron alone	0.013	3.973	0.923

Competitive adsorption of tested herbicides:

Different quantities of atrazine and diuron stock solutions were mixed together, to prepare different initial concentrations of the mixture and constant with soil-liquid ratio (1:10) for each. The competitive adsorption isotherms of atrazine and diuron from binary combination were presented in Fig. (5). Both compounds, atrazine and diuron show isotherms mainly of the S-type. The quantity adsorbed of each herbicide greatly increase against slight increase of the equilibrium concentration in the presence of other compound. It was observed that the affinity of atrazine to sorbe was more on the tested soil than that diuron. The isotherm fitted Freundlich model was exhibited in Fig. (6). The Freundlich adsorption parameters were

presented in Table 2. The K_f values were 0.036 for atrazine, whereas 0.001 for diuron, indicating that the sorption capacity of tested soil was more for atrazine compared to diuron. The $1/n$ values were more >1 for the tested herbicides. The determination coefficients (R^2) were 0.874 and 0.755 for atrazine and diuron, respectively. It was suggested that diuron is a relatively weak sorbing compared to atrazine which is relatively strong sorbing compound. Therefore, in competition system the adsorption of diuron was affected by

competition of atrazine, whereas the sorption of atrazine was less affected by diuron. The same result was obtained by Gao *et al.* (1998) who found that in binary combination of atrazine and bifenox, the adsorption of atrazine was reduced while, the sorption of bifenox was less affected by the competition. Also, Patiero-Moure *et al.* (2010) found that the influence of herbicide diquat on the adsorption of difenzoquat was higher than that of paraquat on difenzoquat.

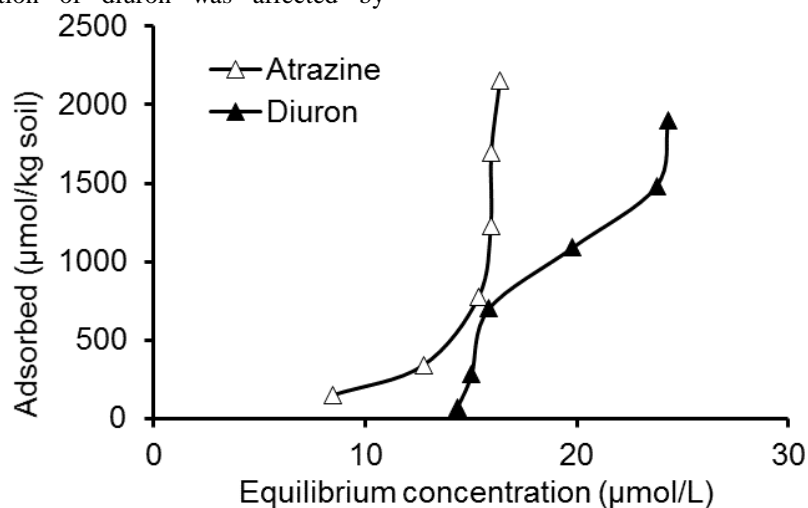


Fig. 5. Competitive adsorption isotherms of atrazine and diuron in their binary combination on clay loam soil

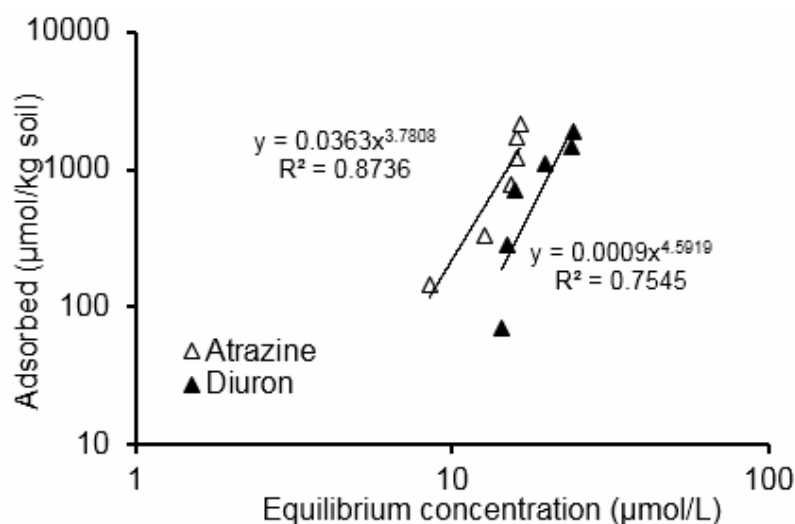


Fig. 6. Competitive adsorption isotherms of atrazine and diuron in their binary combination on clay loam soil fitted in Freundlich model

Table 2. Freundlich competitive adsorption parameters of atrazine and diuron in their binary combination

Compounds	K_f	$1/n$	R^2
Atrazine in binary combination	0.036	3.781	0.874
Diuron in binary combination	0.001	4.592	0.755

In conclusion, the adsorption capacity of tested clay loam soil is more for atrazine individual and in binary combination than that for diuron individual and in binary combination. The adsorption capacity of tested clay loam soil is lower for individual atrazine compared to that in binary combination with diuron. While, the adsorption capacity of tested clay loam soil is higher for individual diuron compared to that in the binary combination. In general, the competitive and non-competitive adsorption of diuron was weak compared to that of atrazine. The sorbing diuron in competitive system was competed for available binding sites and was influenced by the adsorbing atrazine, whereas the sorption of atrazine was less affected by the competition.

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المخلص العربي

الادمصاص التنافسي وغير التنافسي بين مبيد الحشائش أترازين وديورون في التربة الطينية

محمد رياض فؤاد و احمد فرحات الاسود

من الأترازين والديورون بمفرده وكذلك في مخلوط منهما ، ظهر أن السعة الادمصاصية للتربة الطينية اللومية كانت أعلى للأترازين المنفرد أو في المخلوط عن الديورون سواء المنفرد أو في المخلوط. واتضح أيضا أن السعة الادمصاصية للتربة كانت أقل للأترازين المنفرد عنه في المخلوط ، بينما كانت أعلى للديورون المنفرد عن المتواجد بالمخلوط الثنائي. وقد لوحظ أن ادمصاص كلا المركبين سواء بالصورة المنفردة أو بالمخلوط كان أعلى في حالة التركيزات المنخفضة حيث يقل الادمصاص مع زيادة التركيز.

تم دراسة الادمصاص التنافسي وغير التنافسي لمبيد الحشائش أترازين وديورون في التربة الطينية اللومية. أوضحت النتائج المتحصل عليها أن الطول الموجي المناسب لتقدير مبيد الحشائش بجهاز الادمصاص الطيفي هي ٢٢٢ & ٢٨٩ نانومتر وأن قيم ميل خطوط المنحنى القياسي كانت ٠,١٣٢٧ & ٠,٠٠٦١ للأترازين والديورون على الترتيب. وأتضح أن الزمن اللازم للوصول للتوازن هو ثلاث ساعات ، كما اتضح أن ادمصاص كل من مبيد الحشائش تحت الدراسة يتبع معادلة فرنديخ. بمقارنة النتائج المتحصل عليها في حالة الادمصاص التنافسي وغير التنافسي الخاص بكل