Arabian Journal of Chemistry (2013) 6, 121–129

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Application of heated date seeds as a novel extractant for diuron from water

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Received 4 April 2011; accepted 22 July 2011
Available online 30 July 2011

KEYWORDS

Heated date seeds;
Diuron;
Leachability;
SPE;
Principal component analysis

Abstract Diuron has a high leachability with GUS value of 4.1 and a very long residence time in the soil. A novel use of date seeds for diuron adsorption and preconcentration from water is reported. Upon heating at 400 °C, the date seeds exhibited a good adsorption and preconcentration of diuron from water, the adsorption capacity is 2.0 mg/g at 25 °C and pH 7. Using principal component analysis PCA, the adsorption of diuron is correlated to the experimental factors as:

$$K_d(\text{distribution value}) = 0.01(\text{Mass}) - 0.11(\text{pH}) + 0.61(\text{Conc.}) + 0.24(\text{Agt Time}) + 0.49(\text{Temp.})$$

The preconcentration recovery of diuron is also correlated to the experimental factors as:

$$\%\text{Recovery} = 0.09(\text{Samp. vol.}) + 1.76(\text{Mass}) - 4.23(\text{pH}) + 8.06(\text{Eluent vol.})$$

The PCA revealed that initial concentration and temperature are the most significant factors for diuron adsorption. However, pH and eluent volume are the most significant factors for diuron preconcentration. Diuron adsorption is an endothermic process with ΔH value of 8.0 kJ/mol. The shape of diuron isotherm is “C1” type, which is often reported. More than 75% of adsorbed diuron is desorbed using 0.4 M NaOH solution. Diuron at 100 μg/L level can be accurately analyzed using HDS as a solid-phase extractant.

1. Introduction

When pesticides/herbicides enter an aquatic environment, they are exposed to different physical, chemical and microbial processes. Two processes which have a major impact on the fate of pesticides or herbicides are the sorption/desorption processes and biodegradation (Warren et al., 2003). The end of the bath for toxic herbicides in the hydrosphere is strongly determined by their sorption behavior. The chemical reactivity of adsorbed pesticide is significantly different from that in solution (Warren et al., 2003). Herbicides, a branch of pesticides, are commonly detected in natural waters that are close to agricultural regions (Albanis, 1991). The effect of herbicides on the quality of ground and surface waters has become a global issue. Recently,

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Abbreviations: DS, date seeds; HDS, heated date seeds; GUS, Groundwater Ubiquity Score.

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Peer review under responsibility of King Saud University.
doi:10.1016/j.arabjc.2011.07.015

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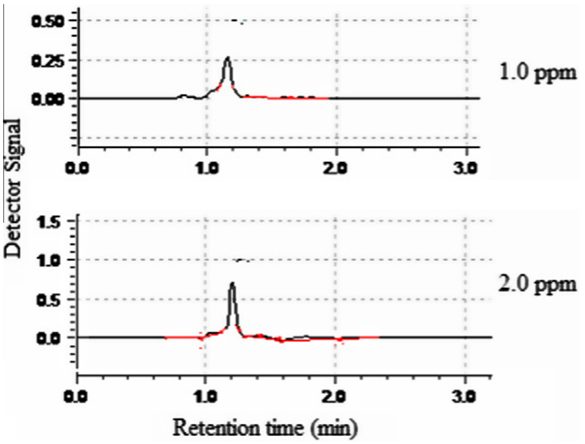


Figure 1 Chromatograms of diourn at two different concentrations.

groundwater contamination by many herbicides has been presented as a serious problem due to their effect on human health (Adachi et al., 2001; Ma and Chen, 2005; Jones and Huang, 2003). Therefore, it is critical to search for new methods for monitoring and removing herbicides from ground and surface waters. Normally, herbicides are not found in natural water in a high level to cause health effects. Instead, they are found in trace amounts, and the concern is for the chronic health problems that may result from prolonged exposure (Adachi et al., 2001; Arias-Estévez et al., 2008). The EPA (Environmental Protection Agency) has established 0.1 μg/L for individual pesticides and 0.5 μg/L for the sum of all pesticides as the maximum allowable limit in fresh water (Ali and Aboul-enein, 2001).

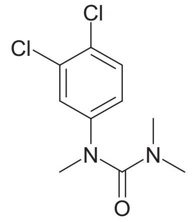
Currently, the main analytical method that is used for pesticides determination is gas and liquid chromatography (Fritz, 1999; Albanis and Hela, 1995; Jiménez et al., 1997; Gong and Ye, 1998; Al-Degs et al., 2009b), however, a preconcentration step is necessary before analysis in many cases. Liquid–liquid extraction was often used for solute preconcentration, but recently solid-phase extraction SPE is becoming popular. Solid-phase extraction is the most common technique for environmental water sample pretreatment because of the large recovery, a large preconcentration factor, short extraction time, low cost, and low consumption of organic solvents (Fritz, 1999; Al-Degs et al., 2009b; Lim, 1988). In SPE, the choice of the adsorbents is the most important factor for obtaining high enrichment efficiency of the target solute. Various types of adsorbents including: C8 (Davì et al., 1999), activated carbon (Jia et al., 1999), cellulose (Valcárcel et al., 2005), multiwalled carbon nanotube (Al-Degs et al., 2009a,b; Al-Degs and Al-Ghouti, 2008), biological substances (Melo et al., 2005), cation-exchangers (Kishida and Furusawa, 2001), and carbonaceous sorbents (Bacaloni et al., 1980) have been tested as adsorbents for pesticides or herbicides.

Local date seeds adsorbent was not tested for removing pesticides (like diuron) from natural water, however, Al-Ghouti and co-workers have evaluated dried date seeds for removing heavy metals and organic dyes from solution and the results indicated the high adsorption capacity of date seeds (Al-Ghouti et al., 2010). In this research, local Jordanian date seeds material is evaluated for removing toxic and leachable diuron from water. Furthermore, the adsorbent is tested as a solid-phase extractant for diuron preconcentration. Principal component analysis is applied to assess the most significant of the examined experimental factors on adsorption/preconcentration of diuron. As a natural biomass, date seeds material is not expensive and easily available.

2. Experimental

2.1. Chemicals and solvents

Diuron was purchased from Aldrich® Company with purity more than 99.5%. The solubility in water (25 °C) is 36 mg/L, water/*n*-octanol partition coefficient at 25 °C ($\log K_{ow}$) is 2.58 (PAN Pesticides Database). The chemical structure of diuron is given below:



Diuron Structure

Standard stock solution of diuron was prepared by dissolving an appropriate amount in distilled water, diluted to 1 L, and the final pH was adjusted to 7.0. Diluted solutions were prepared from the stock solution. All solutions were kept in a dark and cold place. The other chemicals and solvents were of analytical or HPLC grades and obtained from TEDIA (Ohio, USA).

2.2. Determination of Diuron by liquid chromatography and UV-spectroscopy

Quantification of diuron was performed on a phenomenox prodigy C_{18} column. The mobile phase was 50:50 (acetonitrile/water) and the flow rate was 1.0 ml min^{-1}. Diuron was detected using a photodiode array detector (Hitachi High Technologies Co., Japan). Injection volume was 20 μL and all measurements were carried out at room temperature. A linear response ($r^2 = 0.9982$) between diuron content and its beak area ($S_{\text{area}} = 517.3\ C_{\text{diuron}} + 14.8$) with a good dynamic range: 0.2–9.0 mg/L. Using chromatographic method, a detection limit ($S/N = 3$) of 0.12 mg/L is possible. Fig. 1 shows the obtained chromatograms of 1 and 2 mg/L diuron.

At high levels (> 3 mg/L), diuron was simply quantified using UV-spectroscopy (Cary 50 UV–Vis spectrophotometer, Varian, USA) at wavelength of maximum absorption (247 nm). Beer's law is obeyed in the concentration range 1.0–10.0 mg/L with a high degree of correlation, $r^2 = 0.9992$. The earlier analytical method is sensitive for diuron with 0.4 and 1.0 mg/L as the detection limit ($3\sigma_{\text{blank}}$), and limit of quantification ($10\sigma_{\text{blank}}$), respectively.

2.3. Conditioning of raw date seeds

The fruit (the date) is available in the Jordanian markets with the trade name *Al-Majhol*. Five hundred grams of the date was purchased from a local market, the fruit was removed and the seeds were collected. The seeds were washed thoroughly with water, heated at 100 °C, and then ground to fine participles (< 45 μm). The initial investigations showed that date seeds material is not effective for diuron removal. Therefore, 50 g of the powder material was heated under N_2 gas at 200, 300, 400, and 500 °C for 45 min in a special muffle furnace. The aim of pyrolysis was to activate the adsorbent surface and improve diuron adsorption. The adsorbent was further activated by washing with 0.4 M HCl and finally washed with distilled water until neutral washing was obtained. As will be proved later, date seeds material activated at 400 °C was effective for diuron uptake and selected for doing all adsorption and preconcentration studies and will be referred to as HDS throughout this work. The point of zero charge pH_{ZPC} of HDS was estimated as outlined in (Al-Degs et al., 2008). FTIR spectrum of HDS was recorded between 4000–400 cm^{-1} using a PerkinElmer instrument, Nicolet model. The elemental analysis of HDS was carried out using EuroVector EA3000 Instrument (Italy).

2.4. Adsorption/desorption of diuron using HDS

Adsorption isotherm of diuron at 25 °C was measured at different initial concentrations according to the following experiment: 400 mg HDS was added to 250 mL volumetric flasks containing 50 mL of diuron solution of varying concentrations 4–20 mg/L. The flasks were sealed and placed in a thermostated shaker (GFL 1083, Germany) for 7 days to attain equilibrium. After equilibrium, the adsorbent was separated from solution by centrifugation (Hermle-z 200A, Germany). The remaining concentration of diuron solution was quantified. Using single-point adsorption test at 15 mg/L diuron, effect HDS mass, pH, contact time, and temperature on adsorption were studied. Using similar experimental conditions, effect of heat treatment of date seeds on diuron adsorption was studied. For desorption studies, three eluents were tested: H_2O, 0.4 M HCl and 0.4 M NaOH. Initially, 50 mL of 15 mg/L diuron was agitated with 40 mg HDS for 3 days. After equilibrium, the adsorbent was removed by centrifugation, washed with water, placed in 50 mL of the desorption solvent and agitated again for 3 days and the desorbed amount of diuron was determined.

2.5. Diuron preconcentration from natural waters

Solid-phase extraction was carried out using a simple apparatus consisting of a glass column of dimensions (20 cm length × 1 cm diameter). The bottom of the column was plugged with glass wool. Effect of HDS mass, volume of solution, elution volume, pH, and water type on herbicide preconcentration was studied. Typically, 500–1000 mL of water sample was spiked with diuron and passed through the column at a flow rate of 7.0 mL min^{-1} (under gravity). After completion of extraction, the extractant was washed with distilled water to remove any co-adsorbed substances. The trapped solute was eluted with 0.4 M NaOH and the amount of the collected herbicide was directly quantified. Extraction of diuron from natural samples including tap and well waters was studied. Tap water was obtained from our laboratory while well water was obtained from a local well located near Al-Zarqa area. Prior to spiking, the samples were filtered using a special membrane (0.45 μm) to remove any suspended colloids.

2.6. Principal component analysis of adsorption/ preconcentration results

Many factors affecting adsorption/preconcentration of diuron were studied. The combined influence of these factors can be elucidated using principal component analysis. By conducting 29 adsorption experiments, the effect of five factors (HDS mass, solute concentration, pH, agitation time and temperature) on diuron adsorption was studied. Accordingly, a matrix of dimension 29 × 5 and a response vector (K_d values) of dimension 29 × 1 were obtained. Similarly, for preconcentration studies four factors were investigated (sample volume, HDS mass, pH, and eluent volume) and a matrix of dimension 21 × 4 and a response vector (%recovery) of dimension 21 × 1 were obtained. The earlier data were subjected to principal component analysis for assessing the effect of each factor on adsorption/preconcentration of diuron. Principle component analysis PCA is a powerful statistical method that is used for factor analysis, clustering of objects and also for modeling purposes (Brereton, 2003). Principal component analysis PCA was carried out using as outlined in the literature (Brereton, 2003) by using Matlab® (version 7).

3. Results and discussion

3.1. Effect of heat treatment of date seeds on diuron adsorption

In fact, the raw material was inactive for adsorption. To improve diuron adsorption, the adsorbent was heated at different temperatures and then treated with HCl prior to diuron adsorption. The obtained K_d values were 1.8, 2.3, 2.5, and 2.6 L/g, which correspond to the surface heating temperatures of 200, 300, 400, and 500 °C, respectively. K_d values were estimated using the Eq. (2). It seems that, the performance of date seeds was improved by temperature. The performance of the adsorbent was reach to a steady level between 400 and 500 °C. Based on that, 400 °C was selected as the optimum temperature for activating date seeds material. Heating at higher temperatures (i.e. more than 500 °C) was avoided to prevent the carbonization process and creation of a highly porous structure. Migration of diuron within the high porous structure would make elution a hard step. Effect of surface heat treatment on the adsorption of different solutes is a well studied subject and in many cases the performance of the adsorbent is increased upon surface heating (Mazet et al., 1994). Furthermore, acid treatment will improve the chemical properties of date seeds and hence improve diuron uptake. Effect of heat treatment on the magnitudes of surface area and porosity of date seeds is still under investigation in our laboratory.

3.2. HDS characterization

The zero point of charge of HDS was determined following the procedure outlined in (Al-Degs et al., 2008) and was found to be 5.8 as obtained from the pH–mass HDS plot. The surface functional groups of HDS react with water to give acid/basic characteristics of the adsorbent. The combined influence of all surface functional groups determines pH_{zpc}. At solution $pH < pH_{zpc}$, the HDS surface has a net positive charge due

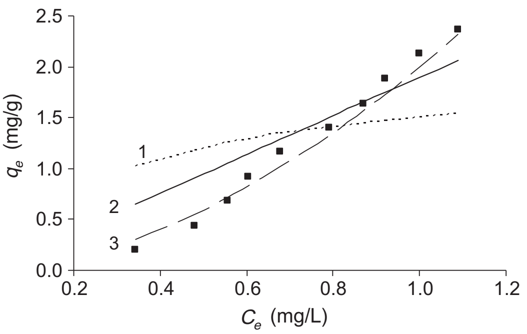


Figure 2 Adsorption isotherm of diuron at 25 °C (mass of HDS: 40 mg, volume of solution 50 mL, pH 7, and shaking time 7 days). (1) Longmuir's model, (2) Henry's model, and (3) Ferundlich's model.

to protonation, while at pH > pH_{zpc} the surface has a net negative charge due to ionization (Al-Degs et al., 2008). The surface functional groups of HDS were detected by FTIR. The main FITR bands were: 3743, 2925, 2360, 1741, 1652, 1515, 1465, and 672 cm^{-1}. The bands at 3743, 2925, 1652, and 1465 cm^{-1} are attributed to vibrational frequencies of the carboxylic acid group. Specifically, the band 2925 cm^{-1} is attributed to –OH of carboxylic acidic group and the band 2360 cm^{-1} is attributed to –C–O stretching. In fact, the presence of carboxylic and hydroxylic groups is essential for herbicides attraction from solution if the electrostatic mechanism is involved. The adsorbent contains 49% C and 10% H as indicated from the elemental analysis of HDS.

3.3. Adsorption behavior of diuron by HDS and comparison with other adsorbents

The amount of removed diuron (q_e mg/g) and the equilibrium distribution value K_d were estimated as follows (Al-Degs et al., 2008):

$$q_e = \frac{(C_0 - C_e) \times V}{\text{mass of adsorbent (g)}} \tag{1}$$

And,

$$K_d = \frac{q_e}{C_e} \tag{2}$$

Where C_0, C_e, and V are the initial concentration (mg/L), equilibrium concentration (mg/L) and solution volume (L). K_d values higher than 1.0 L/g indicates a high adsorption affinity. Adsorption isotherm of diuron at 25 °C is shown in Fig. 2. Adsorption properties of diuron by other adsorbents are summarized in Table 1.

Adsorption isotherm of diuron was measured using the concentration-variation method at 25 °C as shown in Fig. 2. From Fig 2, the shape of the diuron isotherm is "C1"according to Gilles classification for isotherms (Giles et al., 1960). In this isotherm, a constant distribution value is obtained over the studied concentration range, i.e. linear adsorption behavior. This behavior is attributed to the fact that the amount of added diuron was lower than the maximum adsorption capacity of the adsorbent and if all active sites were filled a "C2" isotherm would be observed. Table 1 summarizes the shapes of isotherms that were reported for diuron adsorption (Yang et al., 2004; Bouras et al., 2007; Ramón et al., 2007; Ayranci and Hoda, 2005; Sheng et al., 2005). As indicated in Table 2, the majority of adsorption isotherms were of "L1" or "L2" shape while the "C1" shape is observed in few cases like natural soil and HDS. Adsorption data presented in Fig 2 were modeled using Henry's equation $q_e = K_H C_e$, Freundlich's equation $q_e = K_F C_e^n$, and Langmuir's equation $q_e = QK_L C_e/(1 + K_L C_e)$ (Al-Degs et al., 2008; El-Barghouthi et al., 2007). The adsorption data were fitted to the earlier models using nonlinear fitting methodology. As shown in Fig 2, the Ferundlich equation satisfactorily presented adsorption data while the other models were not applicable. The assessment of the employed models for fitting the diuron isotherm was further made by calculating the sum of square errors squared (SSE). Lower values of SSE indicate better fit to the isotherm. SSE is equal to $\Sigma(q_{t,exp} - q_{t,calc})^2$, where q_e, exp and $q_{e,calc}$ are the experimental and the calculated values of q_e. The SSE values were 0.11, 0.82, and 3.11 for Freundlich, Henry, and Langmuir models, respectively. The earlier SSE values indicated that Freundlich equation was the best. The parameters of the Ferundlich model were K_F = 2.0, n = 1.75, and r^2 = 0.9991. As $n > 1$, then favorable adsorption occurred. The performance of HDS was compared with the other adsorbents. Table 2 summarizes the results which were collected from previous investigations (see Table 1). As can be noted from Table 1, commercial activated carbon has a large adsorption for diuron, 279 mg/g. However, activated

Table 1 Adsorption capacities and shapes of diuron by other adsorbents.

Adsorbent	References	Experimental conditions	Adsorption capacity (mg/g)*	Isotherm shape
Activated carbon	Yang et al. (2004)	pH 4–5, 25 °C	279.0	H2
Wheat-activated carbon	Yang et al. (2004)	pH 4–5, 25 °C	34.1	L2
Surfactant-modified clay	Bouras et al. (2007)	pH 6, 25 °C	0.4	–
Fiber-activated carbon	Ramón et al. (2007)	pH 7, KCl 0.01 M	667.0	–
Cloth-activated carbon	Ramón et al., 2007	pH 7, KCl 0.01 M	870.0	–
Grains-activated carbon	Ramón et al. (2007)	pH 7, KCl 0.01 M	316.0	–
Cloth-activated carbon	Ayranci and Hoda (2005)		213.1	L2
Natural soil	Sheng et al. (2005)	pH 6, 25 °C	0.012	C1
Wheat char	Sheng et al. (2005)	pH 6	8.0	L2
Char-amended soil	Sheng et al. (2005)	pH 6, 25 °C	0.085	L1
HDS	This study	pH 7, 25 °C	2.0	C1

* The reported adsorption capacities were obtained from Langmuir equation. The adsorption capacity of HDS was estimated from one point (at 15 mg/L and 25 °C) due to invalidity of Langmuir equation to adsorption data (See Fig. 1).

Table 2 Variations in K_d with experimental parameters.*

Parameter	K_d (L/g)	Conditions
HDS mass (mg)		Vol.: 50 mL, conc.: 15 mg/L, pH: 7.0, shaking: 3 days, T = 25 °C
50	1.1	
250	1.3	
400	1.9	
750	2.1	
pH		
3.0	2.4	Vol.: 50 mL, conc.: 15 mg/L, mass: 400 mg, shaking: 3 days, T = 25 °C
7.0	1.5	
11.0	1.6	
12.0	0.5	
Initial concentration, mg/L		
1	0.1	Vol.: 50 mL, mass: 400 mg, pH: 7.0, shaking: 3 days, T = 25 °C, pH: 7.0
2	0.5	
3	1.6	
5	1.5	
7	2.2	
9	2.4	
13	2.1	
17	3.2	
20	4.3	
Agitation time, day		
0.5	0.8	Vol.: 50 mL, conc.: 15 mg/L, mass: 400 mg, T = 25 °C, pH: 7.0
1	1.3	
2	1.5	
3	1.7	
4	2.0	
5	2.8	
6	3.3	
7	4.9	
Temperature, °C		
25	2.0	Vol.: 50 mL, mass:400 mg, shaking: 3 days, pH: 7.0. conc.: 15 mg/L
30	2.6	
40	3.0	
50	3.1	

[*] Results are average of three trials, RSD 0.8–2.6%.

carbon is a very expensive material and there are many attempts to replace it by less-expensive adsorbents. Also, the cloth-activated carbon was very effective for diuron uptake with a maximum removal capacity of 870 mg/g. Even though the adsorption performance of HDS is modest compared to activated carbons, but it was much higher than other natural materials like: surfactant–modified clay, natural soil, and char-amended soil. It is important to observe that activated carbon and carbon-based materials have a large adsorption for diuron compared to other materials like clay and natural soil and this is attributed to the favorable hydrophobic–hydrophobic interactions between diuron and activated carbon. The adsorption of diuron by HDS is attributed to the hydrophobic interaction between diuron molecules and the carbonaceous HDS adsorbent (C ~ 50%). The electrostatic interaction, however, is not possible because diuron is a non-ionisable molecule.

3.4. Estimation of GUS value of diuron from adsorption data

Generally, the interaction of herbicides within the soil is highly possible due to the presence of organic matter (Al-Degs and Al-Ghouti, 2008). Moreover, the photodegradation of herbicides by sunlight is also possible under certain conditions (Helliwell et al., 1998). The persistence of herbicides in the environment is highly dependent on their chemical stability and their mobility. The chemical stability is inversely related to the rate of degradation and the mobility is related to the transportation rates in the soil. The earlier two aspects may overlap; if the degradation process is rapid (i.e. unstable compound), then mobility becomes less effective. If the transport process is fast, then different degradation processes may operate as the solute moves to a new environment. Leachability of a herbicide is its tendency to remain chemically stable while moving to groundwater. Leachability is determined by calculating Groundwater Ubiquity Score GUS index (Al-Degs et al., 2008):

$$\mathrm{GUS} = \log(t_{1/2}^{\mathrm{soil}}) \times (4 - \log K_{\mathrm{OC}}) \tag{3}$$

Where $t_{1/2}^{\mathrm{soil}}$ and K_{OC} are the half-life time (in days) and the water/organic carbon distribution coefficient of the herbicide, respectively. If GUS < 1.8, then the herbicide has low leachability (may degrade rapidly or strongly adsorbed) and If GUS > 2.8 the herbicide has a high leachability (may be a stable biocide or has a low K_{OC} value). The values of K_{OC} and $t_{1/2}^{\mathrm{soil}}$ are 499 g/ml and 1367 day, respectively (PAN, Pesticides Database). In fact, diuron has a long residence time (about 3 years) and has a high adsorption capacity toward soil. The GUS value for diuron is 4.1 and this value reflects the high leachability and toxicity of this herbicide. Therefore, monitoring of this compound is necessary.

3.5. Desorption of diuron from HDS

For proper use of HDS as a solid extractant, desorption of diuron should be tested. The nature of the interaction between diuron and HDS may be identified from the outputs of desorption studies. The percent of desorption was calculated from the following equation (El-Barghouthi et al., 2007):

$$\%\mathrm{Desorption} = \frac{\text{amount of eluted pesticide}}{\text{total amount of adsorbed pesticide}} \times 100 \tag{4}$$

The %Desorption values of diuron by H_2O, 0.4 M HCl, and 0.4 M NaOH were 0.1%, 0%, and 75%, respectively. It seems that elution of diuron was not successful using water and acidic solutions. However, 75% of adsorbed diuron was removed using 0.4 NaOH. Many organic solvents like ethanol, acetic acid and diethyl ether were tested, however, no elution was observed. It seems that 25% of the adsorbed diuron was chemically retained on the surface and can not be easily removed and 75% of the adsorbed diuron was physically retained on the surface. The possible mechanism of diuron desorption at basic conditions is mainly attributed to the diuron degradation under basic conditions (Helliwell et al., 1998).

3.6. Effect of experimental variables on diuron adsorption

Diuron adsorption by HDS was investigated under different experimental variables and K_d values are summarized in Table 2.

The following conclusions would be drawn from Table 3: (a) favorable adsorption was observed at higher HDS mass, K_d value has been increased from 1.1 (at 50 mg HDS) to 2.1 (at

Table 3 Preconcentration of diuron (100 µg/L) at different experimental conditions (results are the average of three trials, %RSD 1.3–5.4).

Sample volume (mL)[a]	Detected concentration (mg/L)	%Recovery	Preconcentration factor
250	1.1	44.3	11
500	1.3	26.0	13
750	1.4	18.7	14
1000	1.5	15.3	15
Eluent Volume (mL)[b]			
5	1.0	5.2	11
10	1.5	14.8	15
15	1.5	23.1	16
25	1.9	47.5	19
35	2.0	70.3	20
40	2.3	91.3	23
HDS Mass (mg)[c]			
1.0	1.1	45.3	11
2.0	1.5	59.1	15
3.0	1.6	63.9	16
5.0	1.8	73.7	19
8.0	2.2	86.5	22
10.0	2.3	91.0	23
pH[d]			
2	1.3	103.9	13
4	1.2	95.7	12
7	1.1	89.2	11
10	0.6	47.0	6
12	0.4	32.1	4

[a] Mass of HDS 2.0 g, eluent (0.4 M NaOH) volume 10 mL, extraction flow rate (under gravity action) 7 mL/min, 25 °C, elution flow rate 7 mL/min, and pH = 7.

[b] Mass of HDS 2.0 mg, sample volume 1000 ml, 25 °C, extraction and elution flow rates (gravity) 7 mL/min, and pH = 7.

[c] Sample volume 1000 ml, Extraction and elution flow rates (gravity) 7 mL/min, eluent volume 40 mL,25 °C, and pH = 7.

[d] Mass of HDS: 2.0 g, extraction and elution flow rates 7 mL/min, 25 °C, eluent volume 40 mL, and sample volume 500 mL.

750 mg HDS). K_d was not significantly increased after 400 mg, accordingly, the optimum HDS mass was kept at 400 mg, (b) diuron adsorption was high at pH 3 ($K_d = 2.4$) and highly decreased at pH 12 ($K_d = 0.5$). A good adsorption was observed at pH 7 and 11 with K_d values between 1.5 and 1.6. At pH 3, the adsorbent will be positively charged ($pH_{zpc} = 5.8$) and strong interactions would occur with the diuron electronic π-system. At pH 12, the surface will be negatively charged and this will retard diuron adsorption. Within the range of 7–11, the mechanism of interaction seems to be hydrophobic–hydrophobic type. The interaction of diuron with HDS was good at pH 7 ($K_d = 1.5$), therefore, subsequent studies were conducted at pH 7 and there was no need to maintain highly acidic condition, (c) K_d value of diuron was increased with initial concentration and this correlated with the obtained "C1" isotherm, i.e. linear adsorption behavior. Diuron adsorption was more favorable at longer contact times and this supports the fact that diuron molecules may get deep inside the pores of HDS. However, for practical purposes 3 days was selected which is enough to get good uptake for diuron ($K_d = 1.7$ L/g at 3 days), and (e) diuron adsorption is an endothermic process, K_d value has been increased with temperature. The apparent enthalpy of adsorption (ΔH) and entropy value (ΔS) were calculated using van't Hoff equation (Al-Degs et al., 2008) and found to be 8.0 kJ/mol and 53.6 J mol^{-1} k^{-1}; respectively. Based on ΔH value, diuron adsorption by HDS appears to be a physical adsorption process (Al-Degs et al., 2008).

3.7. Preconcentration and determination of diuron using HDS

The normal concentration of herbicides in the environmental samples is usually around 10–100 µg/L and may be less in some cases. Based on that, the adopted analytical methods (HPLC and UV-spectroscopy) are rather limited for direct quantification of diuron when present at µg level. As shown earlier, HDS was an effective adsorbent for diuron from diluted solutions where very high K_d values were obtained. Therefore, this extractant should be tested for preconcentration/determination of diuron when present at trace levels. The performance of HDS for preconcentration 100 µg/L diuron was assessed under different experimental variables. At 100 µg/L, the direct determination of diuron by liquid chromatography (DL 120 µg/L) or spectroscopic method (400 µg/L) is not possible. The preconcentration factor PF was calculated as follows (Fritz, 1999):

$$\text{preconcentration factor(PF)} = \frac{Vs}{Ve} \times \text{recovery} \tag{5}$$

Where V_s and V_e are the initial sample volume and the eluent volume, respectively. High PF value indicates better preconcentration conditions (Fritz, 1999). Table 3 summarizes the results.

One of the most important variables that affect solute recovery is the sample volume. Less analysis time is needed for small samples. In contrast, a high PF is obtained for a large sample volume as indicated in the Eq. (5). As can be noted from Table 3, the maximum %recovery of diuron was observed at 250 mL. As the sample volume increased, the %recovery decreased and PF increased. The maximum PF was 15 and was obtained at 1000 mL. It seems that the elution volume (10 mL) was not large enough to elute diuron molecules. Generally, the reported preconcentration factors (11–15) were modest and higher factors could be obtained at more optimized conditions. In any SPE procedure, it is necessary to elute most of the retained material in order to obtain the highest recovery and PF. %recovery of diuron was examined at different volumes of 0.4 M NaOH. The results indicated that %recovery and PF were increased at higher NaOH volumes. As shown in Table 4, PF was doubled when the eluent volume was increased from 5 to 40 mL and this is expected because more elution of diuron will occur. Besides the eluent volume, HDS mass is an important factor that affects recovery and preconcentration of diuron. As indicated in Table 3, both %recovery and PF were significantly improved with HDS mass. A %recovery of 91 and PF of 23 were achieved when using 10.0 g HDS. As the HDS mass increased, the number of active sites increased and accordingly more adsorption and recovery is achieved. Finally, the %recovery was high under acidic and neutral conditions and low at basic conditions and the behavior was noted in the earlier equilibrium investigations. At pH 12, PF was only 4 which indicated a negative influence of OH$^-$ ions on diuron enrichment. Generally,

Table 4 Correlation matrix (r^2 values) obtained for adsorption/preconcentration experiments.

	K_d	HDS mass	pH	Conc.	Agit. time	Temp.
Adsorption experiment						
K_d	1.000					
HDS mass	0.318	1.000				
pH	−0.456	0.007	1.000			
Conc.	0.678	−0.024	0.055	1.000		
Agit. time	0.789	0.007	−0.017	0.058	1.000	
Temp.	0.437	0.010	−0.022	0.076	−0.023	1.000
Preconcentration experiment						
	%Recovery	Samp. vol.	HDS mass	pH	Eluent vol.	
%Recovery	1.000					
Samp. vol.	−0.507	1.000				
HDS mass	0.658	−0.072	1.000			
pH	−0.710	0.000	0.000	1.000		
Eluent vol.	0.414	−0.058	−0.021	0.000	1.000	

preconcentration of diuron could be carried out at pH 2–7 where high %recovery (89–104) and PF (11–13) are observed.

3.8. Principal component analysis of adsorption/preconcentration results

Before running PCA, the degree of correlation between the factors and between the factors and K_d or %recovery were evaluated by estimating correlation matrix of the data presented in Tables 4 and 5. The results are shown in Table 4.

As can be noted from Table 4, there is no positive or negative correlation among the studied factors for both experiments and this is obvious from the very small r^2 values. For example, in the preconcentration experiment the correlation coefficients between HDS mass and pH or sample volume were zero which is expected because these factors are independent of each other and this is true for other factors. However, there is some correlation between K_d and %recovery with the studied factors. For the adsorption experiment, the maximum correlation was observed for agitation time/K_d and diuron content/K_d, 0.678 and 0.789, respectively. However, for the preconcentration experiment the maximum correlation values were observed for HDS mass and pH, which showed a negative correlation with %recovery (−0.710).

The data presented in Tables 4 and 5 were subjected (separately) to PCA to derive an empirical relation between the factors and K_d or %recovery. Initially, the data were mean-centered prior to analysis and the following empirical equations were obtained:

$$K_d = 0.01(\text{Mass}) - 0.11(\text{pH}) + 0.61(\text{Conc.}) + 0.24(\text{Agt Time}) + 0.49(\text{Temp.}) \quad (6)$$

$$\%\text{Recovery} = 0.09(\text{Samp. vol.}) + 1.76(\text{Mass}) - 4.23(\text{pH.}) + 8.06(\text{Eluent vol.}) \quad (7)$$

Student's t-test was used as a statistical indicator to assess the significance of each factor in the earlier relations provided that more experiments were performed than the number of factors. The significance t-test was carried out as follows (Brereton, 2003): (a) the square covariance matrix was calculated for both systems and the variances (v) (the diagonal values of covariance) were obtained, (b) S_E, the error sum of squares, which were calculated from the experimental/true values and the predicted values, (c) determination of mean error sum of squares (s) by dividing S_E by number of degrees of freedom which equals to $N-P$, where N is number of experiments and P is the number of factors, and (d) estimation of t-value, $t = \frac{b}{(sv)^{1/2}}$ and the higher this ratio, the more significant is the factor at the desired confidence level. The obtained v and t values were summarized in Table 5 for both experiments.

Table 5 Significance t-test for the importance of experimental factors.

Factor	Coefficient	v	t
Adsorption experiment[a]			
HDS mass	0.01	9877.6	0
pH	0.11	2.1	0.12
Conc.	0.61	22.7	0.02
Agit. time	0.24	1.5	0.31
Temp.	0.49	9.9	0.25
Preconcentration experiment[b]			
Samp. vol.	0.09	19079.2	0
HDS mass	1.76	5.3	0.20
pH	4.23	4.0	0.53
Eluent vol.	8.06	43.7	0.31

[a] $S_E = 8.5$, $s = 0.37$, and $N–P = 24$.

[b] $S_E = 38.3$, $s = 2.39$, and $N–P = 17$.

The tabulated t values at 24 degrees of freedom (for adsorption experiment) and 17 degrees of freedom (for preconcentration experiment) are 1.71 and 1.74 at 95% confidence level, respectively. For both experiments and for all factors, the calculated t values were less than the t_{table} values. Accordingly, all the studied factors have an important affect on diuron adsorption and preconcentration, however, with different magnitudes. As shown in Eqs. 6 and 7, diuron concentration and temperatures are the most important factors (they have the largest coefficients) that affect diuron adsorption. For diuron preconcentration, pH and eluent volume are the most significant factors that affect diuron preconcentration from solution. The prediction power of Eqs. 6 and 7 was further tested by re-estimating K_d and %recovery and the relative error of prediction REP% was calculated for comparison purposes.

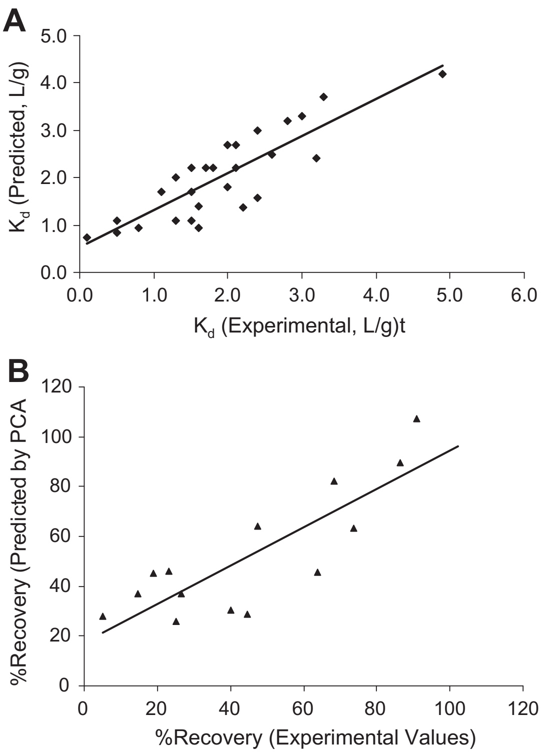


Figure 3 Prediction of K_d (A) and %recovery (B) using PCA.

Fig. 3 shows the plots between experimental and predicted values of K_d and %recovery.

As indicated in Fig. 3, the prediction power of Eqs. 6 and 7 is high; the produced correlation coefficients were 0.7765 and 0.7221 for K_d and %recovery, respectively. The obtained REP% values were 3.0 (for K_d) and 9% (for %recovery) which reflects the high credibility of the derived empirical equations.

3.9. Preconcentration/determination of diuron in natural waters

It is very important to assess the extraction power of HDS in real water samples like tap and well waters where many interferences are present. The interferences that present in real waters would affect diuron extraction/preconcentration. Our earlier studies indicated that extraction efficiency of an adsorbent is decreased when applied for real waters (Al-Degs and Al-Ghouti, 2008; Al-Degs et al., 2009a). The preconcentration of 100 μg diuron was studied using tap and well waters. The other experimental variables were maintained at: sample volume 500 mL, HDS mass 2.0 g, pH 7, and extraction/elution flow rate 7 mL/min. The results of this experiment are presented in Fig. 4.

Generally speaking, the %recovery of diuron has been reduced in natural waters compared to pure water. As shown in Fig. 4, the %recoveries of diuron under the same experimental conditions were: 84.2%, 63.0%, and 42.7% for pure, tap and well waters; respectively. However, diuron preconcentration factors were: 11, 8, and 5 for pure, tap and well waters; respectively. The earlier results indicated the high influence of water interferences on diuron preconcentration. The chemical analysis of water samples are: distilled water contains Cl^- (35 mg/L) and total hardness as $CaCO_3$ (30 mg/L). Tap water contains $Cl^- = 500$ mg/L and total hardness as (600 mg/L).

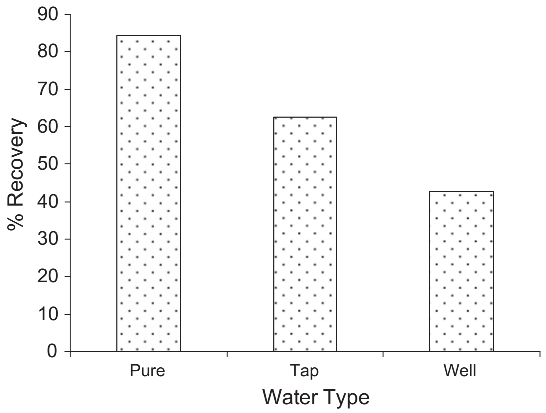


Figure 4 Effect of water type on diuron preconcentration at 100 μg/L.

Well water contains Cl^- 360 (mg/L), total hardness 540 (mg/L) and organic matters (8.3 mg/L). It seems that the high content of common ions and organic matters in well and tap waters have reduced diuron preconcentration. In fact, diuron preconcentration by HDS is a promising process and can be further improved by the surface modification of HDS, which is the subject of our next research.

4. Conclusions

In Jordan, diuron is used in agriculture and hence contamination of ground and surface waters by this compound is highly possible. HDS showed a good adsorption capacity for the toxic and highly leachable diuron herbicide. The adsorption capacity was 2.0 mg/g at pH 7 and 25 °C. Uptake of diuron by heated date seeds was a favorable process where the K_d values were higher than unity over wide experimental conditions. The shape of the diuron isotherm was "C1" which is not common when compared to the other reported isotherms. The process of diuron adsorption has an endothermic nature. Desorption of diuron from HDS was easily attained by 0.4 M NaOH solution. HDS has a good preconcentration power; the experimental results indicated that 100 μg/L of diuron can be extracted with recoveries of 63.0% and 42.7% from tap and well waters, respectively. According to the PCA analysis, diuron concentration and solution temperature are the most significant factors for adsorption and pH and eluent volume are the most significant factors for diuron preconcentration. As a future work, the surface of HDS could be further modified to improve its preconcentration power for diuron and other herbicides.

Acknowledgments

The authors highly appreciated the financial fund of this project from The Hashemite University/The Dean of Research and Graduate Studies (Jordan).

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