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Synthesis of tannic acid azo polyurethane sorbent and its application for extraction and determination of atrazine and prometryn pesticides in foods and water samples

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ABSTRACT

A new inexpensive sorbent (PUF–azo–Tan) was prepared by the coupling of tannic acid with polyurethane foam. The PUF–azo–Tan was characterized using different tools. Two new bands at 1724.1 and 1596.8 cm^{-1} assigned for C=O and N=N groups appeared in the IR spectrum of PUF–azo–Tan. The PUF–azo–Tan contains 0.95 and 0.15 mmol g^{-1} of phenolic and carboxylic groups, respectively. The pH$_{ZPC}$ value of PUF–azo–Tan is 6.4. The PUF–azo–Tan has a considerable stability toward acid, alkali, and organic solvents. Atrazine and prometryn pesticides were extracted and preconcentrate by PUF–azo–Tan column and then analyzed by gas chromatography (GC) coupled with mass spectrometry. The effects of different parameters including pH, sample volume, temperature, initial concentration of pesticides, and shacking time were studied to optimize the presented procedure. The sorption capacity of PUF–azo–Tan was 0.14 mmol g^{-1} (32 mg g^{-1}) and the extraction of the pesticides was accomplished within 3–5 min. Kinetics studies data fitted the pseudo-second-order model ($R^2 = 0.989$). The average detection limit of triazine pesticides in solution was 0.6 ng mL^{-1} (RSD = 0.35%, $n = 3$). The equilibrium process was well described by the Freundlich isotherm model ($R^2 = 0.993$). The extraction of the tested pesticides was accomplished in a period range 3–5 min. The proposal study reveals PUF–azo–Tan has the potential of application as an efficient sorbent for the extraction and preconcentration of pesticides in cucumber, guava and potato foods, and water samples.

1. Introduction

The application of pesticides in agricultural practices is a well-established method of controlling weed growth and reducing the loss of crop caused by insects, microbes, and other pests (Chelme-Ayala et al., 2010; Deng et al., 2014; Deme et al., 2014). Triazine derivatives e.g., atrazine and prometryn pesticides are among the most widely and frequently used, and they are the mostly found organic pollutants in natural water (Environmental Protection Agency, 2006). Atrazine and prometryn are used to stop pre- and post-emergence broadleaf and grassy weeds in major crops (USEPA, 2004). These compounds are both effective and inexpensive, so they are well-suited for production systems with very narrow profit margins, as in maize crop. They are slightly too moderately toxic compounds which are classified as a member of toxicity class II or III, depending on the formulation (Environmental Protection Agency, 1996). The pesticides are suspected of causing cancers, birth defects, and disruption of hormone function (LeDoux, 2011).

The analysis of pesticides in food and wastewater samples usually involves many steps including their extraction from the matrix, subsequent clean-up of the extracts, and finally chromatographic analysis (Korba et al., 2013; Giannoulis et al., 2014a; Campo et al., 2013). Consequently, sensitive pretreatment techniques are required for the determination of trace pesticides in water, soil, and plant samples (Wang et al., 2013; Bolanos et al., 2007). Several methods have been described for the extraction of pesticides e.g., supercritical fluid extraction (Goncalves et al., 2006), pressurized liquid extraction (García-Rodríguez et al., 2010), microwave-assisted extraction (Chen et al., 2007), ultrasonic extraction (Goncalves and Alpendurada, 2005), liquid–liquid microextraction (Dasgupta et al., 2011), and solid-phase extrac-

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tion (Kim et al., 2008). Also, many types of adsorbents e.g., C_{18} bonded silica (Rodrigues et al., 2010), nano-composite material (Zhao et al., 2011), polymer-coated multi-fibers (Basheer et al., 2011), sol–gel (Ebrahimi et al., 2011), activated soil filters (Bester et al., 2011), carbon nanotubes (Pyrzynska, 2011), and polyurethane foam (Moawed and El-Shahat, 2014) have been developed for the recovery of pesticides from aqueous media. Recently, solid-phase extraction has been applied widely to the analysis of environmental, food, biological, and pharmaceutical samples (Giannoulis et al., 2014b; Hou et al., 2014; Arias et al., 2014).

Polyurethane foam (PUF) has a good flexibility, good stability, and high efficiency for the extraction of various inorganic and organic species (Moawed and El-Shahat, 2013; Moawed and Alqarni, 2013). It can be used without pretreatment (Abdel Azeem et al., 2011), immobilized (Robaina et al., 2009), composite (Moawed et al., 2014), incorporation (Moawed et al., 2013), and coupled (Abdel Azeem et al., 2013) with different ligands. In this work, we prepared PUF functionalized with tannic acid through an azo(N=N) group. The acidic character of PUF–azo–Tan makes it suitable for the removal of basic organic compounds e.g., triazine pesticides. The sorption behavior of atrazine ($C_8H_{14}N_5Cl$, 215.68, 1-Chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine) and prometryn ($C_{10}H_{19}N_5S$, 241.36, 2-methylthio-4,6-bis(isopropyl amino)-1,3,5-triazin) pesticides onto the PUF–azo–Tan have been studied to optimize the conditions for the best preconcentration and determination of pesticides. The proposed method has been successfully applied for the extraction of triazine pesticides from food and water samples.

2. Materials and methods

2.1. Apparatus

Atrazine and prometryn were determined employing gas chromatography (GC Varian CP-3800) equipped with a mass spectroscopy (Varian triple quadruple MS/MS 1200L). The pH measurements were carried out using a pH meter from microprocessor pH Meter (HANNA instruments). IR spectra were recorded on a Shimadzu FTIR-8400 Fourier transform infrared spectrophotometer. UV–vis spectra were recorded using a Shimadzu UV-1800 spectrophotometer (Shimadzu Corporation, Japan). Glass columns of about 25-cm long and 1.5 cm in diameter were employed in the chromatographic separation experiments.

2.2. Chemicals and reagents

The stock solutions (1 mg/L) of atrazine and prometryn (Supelco, Bellefonte, PA, USA) were prepared in deionized water. Tannic acid ($C_{76}H_{52}O_{46}$, BDH, Poole, England), HCl (Adwic, El-Naser Pharmaceutical Chemical Co., Egypt), and $NaNO_2$ (Fluka A.G., Buchs, Switzerland) were used. Commercial polyurethane foam (PUF) open-cell polyether-type was supplied from the Egyptian company for foam production, Cairo, Egypt. PUF sheet was solidified in by putting it in a liquid nitrogen reservoir then it was cut into similar cubic plugs ($\sim$0.125 cm^3) by a slicer.

2.2.1. Synthesis of sorbent (PUF–azo–Tan)

Polyurethane foam functionalized with tannic acid (PUF–azo–Tan) was prepared: a 5 g portion of PUF cubes was soaked in 500 mL of HCl (2 mol L^{-1}) for 24 h then washed with water and kept in 0.1 mol L^{-1} HCl in an ice bath. The PUF cubes was diazotized by the drop wise addition and vigorous stirring of 50 mL of $NaNO_2$ (2 mol L^{-1}) to the cold acidic solution containing PUF. The color of PUF cubes turned to pale yellow due to the formation of diazonium chloride. For the coupling step, a cool solution of tannic acid was added dropwise to the diazotized PUF cubes and

the mixture was left for 2 h in the fridge. The yellow PUF–azo–Tan material was washed with distilled water followed by acetone and then air-dried.

2.3. Recommended procedures

The separation of atrazine and prometryn pesticides was carried out by a batch technique at 25 °C. A portion of 0.05 g portion of the PUF–azo–Tan was added to a flask containing 1000 mL solution of the tested pesticides solution (5 µg L^{-1}) in a shaker adjusted to the desired shaking speed (60 rpm). After a certain time, the flasks were removed from the shaker. The final pesticides concentration remaining in the supernatant solution was determined by extracted it three times with 10 mL CH_2Cl_2. The extract was evaporated to 1 mL and injected in GC. Also, the pesticides concentration recovered from PUF–azo–Tan with 10 mL of CH_2Cl_2 was determined using GC/mass spectroscopy (EPA 619 method). The following equations were used to calculate the sorption percent sorption of pesticides (% E), capacity of sorbents (Q, mg/g) and distribution coefficient (K):

$$\%E = \left(\frac{(C_0 - C)}{C_0} \right) \times 100 \tag{1}$$

$$Q = \frac{(C_o - C)V}{m} \tag{2}$$

$$K = \left(\frac{(C_o - C)}{C} \right) \frac{V}{m} \tag{3}$$

where C_0 and C are the initial and remain concentrations of pesticides in solution, respectively. V is the volume of solution and m is the mass of PUF–azo–Tan.

Pesticides in water samples of Nile River and Mariotia canal were determined using batch method. A 0.05 g portion of the PUF–azo–Tan was mixed with a 1000 mL of water sample (spiked with 5 and 10 mg of pesticides). After shaking for 15 min, the solution was filtered then the concentration of pesticides in solution was determined using GC–MS/MS.

Pesticides in food samples (cucumber, guava, and potato) were prepared using a method similar to that described in previous studies (Gholivand et al., 2012; Tian et al., 2014). An accurately weighed 10 g portions of food samples crushed with a juicer to produce a liquid including juice and scum. The liquid was mixed with 10 mL of water and spiked with 5–10 mg of pesticide in a 150 mL Erlenmeyer flask. After soaking for 15 min, the mixture was homogenized at high-speed stirrer for 2 min with 100 mL of H_2O. A 25 mL portion of the supernatant was mixed with 0.05 g of PUF–azo–Tan and shacked 15 min. The concentration of pesticides was determined by using GC–MS/MS.

2.4. Instrumental determination characteristics

Capillary column VF is 5 ms (5% phenyl-, 95% dimethylsiloxane). Thermal program: 40c (hold 2 min), 250 c (with rate 20 c/min), 280 c (with rate 30 c/min and hold 1 min). MS: sim mode (selective ion monitoring) for each compound. Flow rate is 1.2 mL min^{-1} and injection volume 2 µL.

3. Results and discussion

3.1. Characterization of PUF–azo–Tan

The IR spectrum of PUF–azo–Tan (Fig. S1) showed that broad band at 3621.7–3014.2 cm^{-1} is corresponding to O—H and N—H groups stretching vibration. In addition, two absorption bands are appeared at 1724.1 and 1596.8 cm^{-1} which are assigned to the C=O and N=N groups, respectively (Table 1).

Table 1
Comparison between the characterization of PUF and PUF–azo–Tan.

Property	PUF	PUF–azo–Tan
UV–vis spectra		
λ_{max} (nm)	Nil	237,465
After sorbed FeCl$_3$	Nil	450,966
IR spectra		
υ—OH, NH aromatic (cm^{-1})	Broad band at 3430–3180	Broad band at 3622–3014
υ—CO (cm^{-1})	Nil	1724.1
υ—N=N (cm^{-1})	Nil	1596.8
Elemental analysis, C, H, N, O %	64.0, 9.5, 7.2, and 18.8	61.8, 8.7, 6.1, and 22.8
Color	White	Orange
pH$_{ZPC}$	8.8	6.4
Phenolic group (mmol g^{-1})	Nil	0.95
Carboxylic group (mmol g^{-1})	Nil	0.15
Iodine number (mmol g^{-1})	0.19	0.23
Density (kg m^{-3})	13.5	23.6

The determined pH$_{ZPC}$ value of PUF–azo–Tan was 6.4 (Fig. S2). The result shows that the surface of PUF–azo–Tan is positively charged at pH < 6.4 and is negatively charge at pH > 6.4. The pH$_{ZPC}$ value is based on membrane-like structure and functional groups of PUF–azo Tan e.g., urethane, ether, phenolic, and carboxylic OH groups.

The elemental analysis of PUF and PUF–azo–Tan was studied. The carbon, hydrogen, and nitrogen percentage in PUF–azo–Tan are less than in PUF due to the partial hydrolysis of some urethane groups. The percentage of oxygen in PUF–azo–Tan (22.8%) is more than that of PUF (18.8%) due to the addition of tannic acid (Table 1).

For UV–vis spectrophotometric measurements, a thin film of PUF–azo–Tan ($3.5 \times 0.8 \times 0.2$ cm) was used. There are placed in the path of light in a cell filled with methanol. The result shows that the new two peaks at 237 and 365 nm are appear in PUF–azo–Tan spectrum (Fig. S3). The detection of phenolic group in PUF–azo–Tan was tested by using FeCl$_3$ using UV–vis spectrophotometer. The color of PUF–azo–Tan is changed from orange to violet (λ_{max} = 450 and 966 nm, Fig. S3) after the addition of FeCl$_3$ solution indicates that the PUF–azo–Tan contain phenolic group.

In order to determine the amount of phenolic and carboxylic groups in PUF–azo–Tan, the back titration methods using 0.05 mol L^{-1} NaOH and NaHCO$_3$ solution was applied. The results show that the PUF–azo–Tan contain 0.95 and 0.15 mmol g^{-1} of phenolic and carboxylic groups, respectively. These results indicate that the mainly surface sites of PUF–azo–Tan are acidic groups.

The color of PUF–azo–Tan is changed from orange to red in HCl solution due to protonation of hydrogen ions on the oxygen and nitrogen atoms. The loss of the proton changes the electronic structure of the compound, resulting in a change of color from red to yellow–orange.

To determine the adsorption capacity (iodine number), a 25 mL of iodine solution of 0.05 mol/L was added to 0.1 g of PUF–azo–Tan. The iodine number (mmol/g) was determined after the titration of 10 mL of residual solution with 0.05 mol/L sodium thiosulfate in the presence of 1 mL of 1 wt% starch solution. The sorption capacity of PUF–azo–Tan for iodine was estimated to be 0.23 mmol g^{-1}. The PUF–azo–Tan exhibits better capacity values in comparison to PUF (0.19 mmol g^{-1}).

The densities of the PUF and PUF–azo–Tan were measured; their values are 13.5 and 23.6 kg/m^3, respectively (Table 1). This result indicates that the PUF–azo–Tan is denser than the PUF. The higher density of the PUF–azo–Tan may be attributed to the coupling of PUF with tannic acid.

The chemical stability of PUF–azo–Tan was studied by using different solvents. The results show that the PUF–azo–Tan has a good chemical stability in the presence of concentrated HCl, 6 M H$_2$SO$_4$, 6 M NaOH, conc., NH$_3$, CHCl$_3$ CH$_3$OH, CH$_3$COCH$_3$, and C$_6$H$_6$.
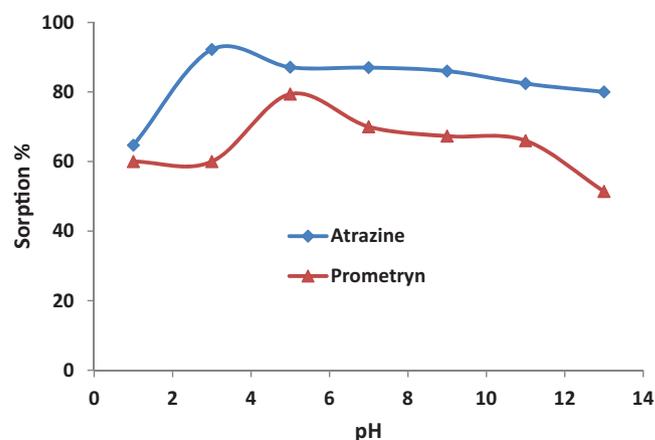
Fig. 1. The pH$_{ZPC}$ of PUF–azo–Tan and the effect of pH on the extraction of atrazine and prometryn onto PUF–azo–Tan.

3.2. Optimum conditions for the extraction of atrazine and prometryn pesticides

The effect of pH on the sorption behavior of atrazine and prometryn pesticides was studied in the pH range of 1–13 using 25 mL sample solution containing individual herbicide. The maximum sorption occurred at pH range from 3–11 to 5–11 for atrazine and prometryn, respectively (Fig. 1). At pH value less than 2.0 the uptake of the studied pesticides is small and then it increases with the increasing of the pH value. The optimum pH value to remove the atrazine and prometryn from aqueous solution is 3 and 5, respectively. The sorption percentage sequence was in order of atrazine > prometryn, this depends on the size of the pesticide molecule.

The effect of initial pesticide concentration on the recovery of atrazine and prometryn by using PUF–azo–Tan was studied. The graph obtained is linear in the range of 0.10–1.16 μg L^{-1} pesticides and correlation coefficient (R^2) are 0.962 and 0.956 for atrazine and prometryn, respectively (Fig. S4). The intercept values of the linear graph are 0.000 and 0.007, respectively. The detection limits for atrazine and prometryn were calculated to be 0.14 and 1.13 μg L^{-1}, respectively. Also, the capacity of PUF–azo–Tan was increased by increasing the initial pesticide concentration then reached a plateau. The sorption capacities of PUF–azo–Tan for atrazine and prometryn were estimated to be 0.18 and 0.11 mmol g^{-1} (38.8 and 26.5 m g g^{-1}), respectively. It is evident from the achieved results that the sorption capacities of the pesticides depend on the size of pesticide molecule. The sorption capacity of PUF–azo–Tan (0.15 mmol g^{-1}) is found to be much better than that of PUF (0.06 mmol g^{-1}).

A precision analysis revealed that the average values of RSD was 0.35% (n = 6) and recoveries percentage values ranged from 97.0% to 101.6%. The limit of detection (LOD = 3σ, where σ is the standard deviation of blank determination) and limit of quantitation (LOQ = 10σ) for atrazine and prometryn were established. The value of LOD of atrazine and prometryn were 0.14 and 1.13 μg L^{-1}, respectively. The LOQ values of atrazine and prometryn were 0.47 and 3.77 μg L^{-1}, respectively. The results of accuracy and precision for the different fortification levels of the pesticides show that the PUF–azo–Tan is suitable for the determination of atrazine and prometryn. The values of LOD and RSD due to the application of PUF–azo–Tan for the determination of pesticides indicate that the PUF–azo–Tan sorbent is more efficient than other sorbents (Table 2) (Galán-Cano et al., 2013; Katsumata et al., 2010; Mendas et al., 2000; Djozan and Ebrahimi, 2008; Tomkins and Ilgner, 2002;

Table 2
Comparison between various sorbents for detection limit of pesticides.

Sorbent	LOD ($\mu g\,L^{-1}$)	RSD (%)	References
Methyl imidazolium–hexafluoro phosphate functionalized silica	0.3, 0.6	10.6	(Galán-Cano et al., 2013)
Multiwalled carbon nanotubes	0.25	6.9	(Katsumata et al., 2010)
C_{18} solid-phase	5	10–12	(Mendas et al., 2000)
Monolithic SPME fiber	20, 68	7.5, 9.5	(Djozan and Ebrahimi, 2008)
Polydimethylsiloxane/divinylbenzene fiber	2–8	–	(Tomkins and Ilgner, 2002)
Combination of liquid membrane and C_{18} solid-phase	10	–	(Khrolenko et al., 2002)
Bamboo charcoal	0.5	8.3	(Zhao and Yuan, 2008)
Piperazine functionalized polyHIPEs	33	–	(Pulko et al., 2007)
Dodecylsulfate-doped polypyrrole film	15	10	(Mohammadi et al., 2009)
Silica fibres coated with polyacrylate	1	–	(Zambonin and Palmisano, 2000)
Tannic acid azo polyurethane foam	0.14, 1.13	0.05, 0.65	This work

Khrolenko et al., 2002; Zhao and Yuan, 2008; Pulko et al., 2007; Mohammadi et al., 2009; Zambonin and Palmisano, 2000).

The influence of shaking time on the recovery percentage of atrazine and prometryn is an importance factor to determine the discrimination order of PUF–azo–Tan behavior toward pesticides. The results obtained show that the extraction of tested pesticides is complete within about 2–5 min shaking time. The equilibrium between atrazine and the PUF–azo–Tan is faster than that of prometryn and PUF–azo–Tan. The proposed method is more fast and efficient than other sorbents (Akhtar et al., 2009; El Bakouri et al., 2009; Zheng et al., 2010).

The effect of temperature on the sorption of atrazine and prometryn onto PUF–azo–Tan was studied. It showed that the sorption of atrazine decreases with increasing the temperature. While the prometryn sorption slight increases with increasing of the temperature. Thermodynamic parameters were evaluated using the following equations: $\ln K = -\Delta H/RT + \Delta S/R$ and $\Delta G = \Delta H - T\Delta S$ where K_c is the distribution coefficient for sorption. The linear plots of $\ln K_c$ vs. $1/T$ ($R^2 = 0.70$) give the values of enthalpy (ΔH) and entropy (ΔS) from the slope and the intercept, respectively. The results obtained show that the sorption of atrazine was better at lower temperature values while the sorption of prometryn is slightly affected with increasing of temperature. The average value of free energy (ΔG) is $-4.5\,kJ\,mol^{-1}$; the negative sign is attributed to the spontaneous nature of sorption process. The values of ΔH for the sorption of atrazine and prometryn are 11.3 and $-2.1\,kJ\,mol^{-1}$, respectively. The negative value of ΔH for prometryn is interpreted as the exothermic chemisorptions process while the positive value of ΔH for sorption of atrazine due to endothermic chemisorptions. The average value of ΔS is $30.6\,J\,K^{-1}\,mol^{-1}$. The positive value of the entropy may be indicative of the faster adsorption of pesticides onto tannic–PUF.

The effect of the sample volume (25–150 mL) to the weight of PUF–azo–Tan (0.1 g) on the uptake percentage (% E) of pesticides was studied using a batch technique. The data indicate that the maximum sorption of pesticides in batch factor (V/m) is 250.

The effect of the eluting volume on the recovery percentage of pesticides was studied. 50 mg of tested pesticides in 25 mL sample volume were shacked with 0.05 g of PUF–azo–Tan for 15 min. The elution of pesticides from PUF–azo–Tan was performed using different volume of CH_2Cl_2 (1–15 mL). The recovery percentages of 97–99% were in 1–5 mL was used for desorption. These results show that the pesticides can be concentrated effectively from the dilute aqueous solutions using PUF–azo–Tan.

3.3. Analytical applications

The analytical applicability of the proposed PUF–azo–Tan was tested for the extraction and determination of atrazine and prometryn in different real samples.

Table 3
Determination of pesticides in water samples using PUF–azo–Tan.

Samples	Added (μg)	Recovery (μg)	
		Atrazine	Prometryn
Nile water	10	9.8	9.3
Wastewater	10	9.3	9.4

Atrazine and prometryn in different samples of wastewater from Mariotia canal in El-Giza city was removed using batch technique. A 50 mL aliquot of water sample (pesticide is not detected) was spiked with standard addition (10–100 μg) of atrazine or prometryn at the adjusted pH. The uptake percentage of pesticides from the water samples onto PUF–azo–Tan were found to be 93–94% ($n = 4$). The results show that the PUF–azo–Tan is a suitable sorbent for the removal of the triazine pesticides from water (Table 3).

Atrazine and prometryn in Nile River water samples were determined using batch method. A 0.1 g portion of the PUF–azo–Tan was mixed with a 25 mL of the samples (spiked with 10 μg of pesticide). The concentration of atrazine and prometryn after recovery with 10 mL of CH_2Cl_2 was determined by GC/MS–MS. The results obtained, shown in Table 3, are in agreement with the values obtained using GC/MS–MS measurements in the central laboratory of GOGCWR. The results show the suitability of the PUF–azo–Tan for water analysis (RSD = 2.6%, $n = 4$).

PUF–azo–Tan was also used for determination of the atrazine and prometryn in food samples (cucumber, guava, and potato). The maximum-likelihood fitting confirmed the agreement between the direct GC–MS/MS and the proposed procedure. Thus, recovery studies were performed and Table 4 shows the satisfactory recoveries of the spiked addition. The results show the suitability of the PUF–azo–Tan for food analysis.

To evaluate the obtained results a strong quality control was performed and the methods were carefully validated (Campo et al., 2013). In water and foods samples, the average recovery of tested pesticides is 93.5% and 81.7% with relative standard deviations 2.6% and 12.9%, respectively. Calibration curves were prepared daily obtaining $R^2 > 0.98$.

Table 4
Determination of pesticides in foods samples using PUF–azo–Tan.

Samples	Added (μg)	Recovery (μg)	
		Atrazine	Prometryn
Guava	10	8.2	9.4
Cucumber	10	6.8	7.8
Potato	10	9.4	7.4
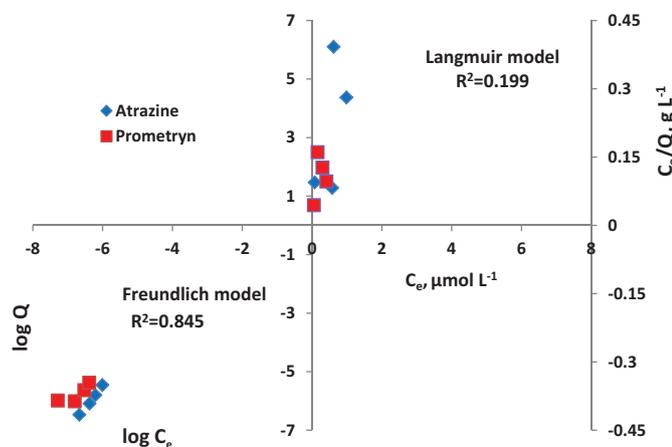
Fig. 2. Langmuir and Freundlich isotherm models for extraction of triazine pesticides.

Fig. 3. Pseudo-first-order and pseudo-second-order kinetic models for extraction of atrazine and prometryn by using PUF–azo–Tan.

3.4. Sorption mechanism

The solvent extraction might be the most probable mechanism of triazine pesticides sorption onto PUF–azo–Tan in acidic medium (pH 2–6). The mechanism based on the triazine compound contains nitrogen atoms, which are capable to form hydrogen bonding with OH groups in PUF–azo–Tan. The pH_{ZPC} value of PUF–azo–Tan is 6.4, therefore, in alkaline medium the surface of the PUF–azo–Tan becomes negatively charged. Accordingly, the triazine pesticide (basic molecule) is adsorbed due to electrostatic interaction of pesticide molecule with the negatively charged surface of the PUF–azo–Tan. Selectivity of PUF–azo–Tan for triazine compounds is attributed to the presence of five basic nitrogen atoms for triazine structure, which make it more basic and more capable of donating electrons. Based on the behavior of triazine pesticide extraction on the PUF–azo–Tan it has been speculated that ion association (Trizine$^+$: [PUF–azo–Tan]$^-$) may be the principal mechanism for the sorption of triazine compounds in pH 6–11.

The plot of Q_c/C_e vs. C_e for the experimental data according to Langmuir model $\left[C_e/Q_c = (1/K_L b) + (C_e/K_L) \right]$ gives a bad linear relationship. The linear plot of $\log Q_c$ vs. $\log C_e$ according to Freundlich $\left(\log Q_c = \log K_F + \frac{1}{n} \log C_e \right)$ is shown in Fig. 2. Comparing the correlation coefficient (R^2) values, the R^2 values for Freundlich model ($R^2 = 0.845$) are higher than those for Langmuir model (Fig. 2, $R^2 = 0.199$). These results indicate that the Freundlich model could adequately describe the adsorption isotherms, which attributed to the heterogeneous surface structure of the PUF–azo–Tan.

The Dubinin–Radushkevich isotherm $\left(\ln Q_c = \ln K_{D-R} - \beta \epsilon^2 \,\&\, \epsilon = RT \ln \left[1 + (1/C_e) \right] \right)$ was tested. The linear plot of $\ln Q_c$ vs. ϵ^2 has correlation values $R^2 = 0.835$. The values of β for sorption of atrazine and prometryn pesticides computed from the slope are –0.008 and –0.003 kJ^2 mol^{-2}, respectively. The value of the sorption energy (activation energy, E) was calculated using equation: $E = 1/\sqrt{-2\beta}$. The values of E evaluated are 7.9 and 13.0 kJ mol^{-1} for atrazine and prometryn, respectively, indicating that the rate of sorption is relatively fast.

The pseudo first order $\left[\log (Q_e - Q_t) = (\log Q_e) - (k_1 t/2.303) \right]$ and pseudo second order $\left[t/Q_t = (1/k_2 Q_e^2) + (t/Q_e) \right]$ kinetic models are tested to fit the experimental data for sorption of atrazine and prometryn. A straight-line plot of t/Q_t vs. t indicates that the process is a pseudo-second-order reaction (Fig. 3). Also, the correlation coefficient R^2 value for pseudo second order sorption model (0.987) is higher than R^2 value for pseudo first order kinetic (0.393, Fig. 3). This suggests that the pseudo-second-order adsorption mechanism is predominant. The rate constant (k_2) was 1.17
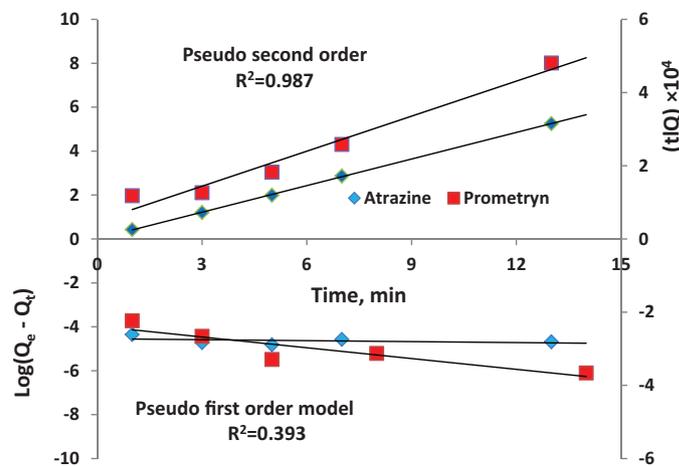
and 0.24 g mmol^{-1} min^{-1} for atrazine and prometryn, respectively. The values of k_2 sequence was in order atrazine > prometryn, which showed that the rate constant depends on the size of pesticide.

The Morris-Weber $\left[Q_t = k_i \sqrt{t} \right]$ models are applied to explain the diffusion mechanism of pesticides onto PUF–azo–Tan where k_i is the intraparticle diffusion rate constant (mmol g^{-1} min$^{-1/2}$). The sorbed atrazine and prometryn concentration Q_t at time t was plotted against the square root of time to test the applicability of the Weber–Morris equation. The obtained results show the rate of diffusion is fast in the early stages of sorption and a linear relationship was verified where the diffusion constant (k_M) was found to be 0.003 and 0.044 µmol g^{-1} min$^{-1/2}$ for atrazine and prometryn, respectively. By extension of shaking period, the relation becomes no longer linear and deviation has been observed.

4. Conclusion

A new sorbent (PUF–azo–Tan) was prepared and used to pre-concentrate and determine triazine pesticides from food and water samples. The developed method is simple, rapid, and easy to use. Also, it is selective and sensitive procedure for the determination of atrazine and prometryn in water and food samples. The kinetics and thermodynamics of the tested pesticides sorption onto PUF–azo–Tan were studied. The negative values of ΔG indicate that the spontaneous of the sorption of pesticides.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.enmm.2015.02.001.

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