

Facile Removal of Pesticides from Aqueous Solutions Using Magnetic Nanocomposites

II. Adsorption experiments and kinetic study

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Using previously presented magnetic inorganic/organic magnetic nanocomposites, the adsorption of two known commercial-available pesticides (active ingredients deltamethrin and thiamethoxam, respectively) was achieved. The differences in adsorption observed can be explained by the reduced affinity of the nitro group in the ionized form from thiamethoxam towards the carboxyl groups from chitosan. From the kinetics studies it was determined that in case of thiamethoxam adsorption process is exothermic in nature, while in the case of deltamethrin the process is endothermic. The Sips isotherm was more suitable to describe the adsorption of pesticides on prepared adsorbents. The maximum adsorption capacity determined for the developed material was 247.12 mg/g (for deltamethrin) and 53.29 mg/g (for thiamethoxam).

Keywords: magnetic nanocomposites, adsorption, kinetic studies

Pesticides are a potential concern for aquatic life and ecosystems, as well as for human health, being a class of water pollutants with a considerably complex structure. They are usually named by their chemical names, active ingredient names or product names. Usually products have active ingredients and adjuvants.

On insecticide's market there are known imidacloprid, thiamethoxam, clothianidin, dinotefuran, acetamiprid, thiacloprid, and nitenpyram. For thiamethoxam there is a lack of literature regarding the removal and degradation from waters comparing with the other compounds, especially using adsorbents with nanostructures. There are some studies the degradation of thiamethoxam in different type of soils [1] and studies which present the potential impacts to aquatic systems [2]. Thiamethoxam is a bio-accumulative compound, with ability to harm liver, kidney and other organs, even at human, and hard to remove [3]. Our group previously demonstrated the influence of thiamethoxam accumulation in physiological indices of *Pelophylax ridibundus* (Pallas, 1771) [4].

Another group of worldwide used pesticides is the class of pyrethroids, with high risk for the aquatic, environment especially for the fishes [5]. This class is divided into two groups according to their chemical structure: type I (alletrin, permethrin, piretrin) and type II (deltamethrin, permethrin) [6]. In the case of deltamethrin, there are studies proving it is a compound which can be bio-accumulated and often toxic [7].

Several published studies describe different methods of degradation or removal pesticides from different classes, such as photocatalysis [8], adsorption [9] or biodegradation [10].

In the present work is described the facile removal of pesticides from the neonicotinoids and pyrethroids classes using magnetic nanoscale core-shell composites, also presenting the kinetic aspects involved in the pesticide up-take.

Experimental part

Pesticides

The registered formulations of two pesticides commonly applied in agriculture were used: Decis Expert 100 EC® (deltamethrin 100 g/L, Bayer, Leverkusen, Germany) and Actara 25 WG (thiamethoxam 25% w/w, Syngenta, Basel, Switzerland).

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Analytical methods

Deltamethrin and thiamethoxam pesticides were determined and quantified by liquid chromatography using an Agilent 1260 Infinity series LC system (Agilent Technologies), equipped with a time-of-flight mass spectrometer (TOF-MS) detector, a quaternary pump and autosampler. Elution was achieved by an isocratic program with the mobile phase consisting of a mixture of ultrapure water with 0.1% acetic acid/acetonitrile (95:5) (v/v) at 0.3 mL/min flow rate.

Deltamethrin and thiamethoxam were quantitatively determined using calibration curves built with the concentrations 25, 50, 100, 200 and 400 ppm. For the highest concentration, 400 ppm, it was necessary a 50% dilution in order to be kept in the linearity domain.

Pesticide solutions and adsorption experiments

The aqueous solutions were obtained by dissolving Decis Expert 100 EC[®] and Actara 25 WG in distilled water, to obtain stock concentrations of 400 mg/L (active substance). All the other concentrations used in the study were obtained by dilution. For the adsorption experiments, the batch technique was applied. A typical experiment was conducted by weighting 0.02 g of adsorbent materials and mixing with 20 mL of pesticide solution (at a concentration of 200 mg/L) into glass tubes. The test tubes were introduced in a test tube rotating shaker (GFL 3025) for different amount of time in order to evaluate the adsorption process evolution in time. The encoding of samples collected at different time are: T1 – 1 hour, T2 – 3 hours, T3 – 5 hours, T4 – 8 hours, T5 – 24 hours and T6 – 48 hours. In order to preserve the relevancy for real conditions, solution pH was adjusted to 7. At the end of the reaction time, tubes content was filtered through 0.45 µm syringe filters and the remaining pesticide content was evaluated using HPLC. Each experiment was carried out in triplicate, and the average values were used as results. The amount of pesticides retained on the adsorbent at a time t was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

where: C_0 and C_t are the initial concentration and the concentration of the pesticide at the time t in the solution (mg/L), V is the volume of the solution (L), and m is the amount of the adsorbent (g) [11].

For the evaluation of the adsorption equilibrium, 0.02 g of adsorbent and mixed with 20 mL pesticide solution (concentrations ranging from 10 to 200 mg/L) into glass tubes for 10 h in order to reach adsorption equilibrium. Adsorption vials content was filtered through 0.45 µm syringe filters and the filtrate was submitted to analysis. Each experiment was carried out in triplicate, and the average values were used as results. The amount of pesticide retained on solid surface was calculated by equation:

$$\frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where: C_0 and C_e are the initial concentration and the concentration of the pesticide at equilibrium (mg/L), V is the volume of the solution (L), and m is the amount of the adsorbent (g) [12].

Results and discussions

According to literature and NIST mass spectra, the main five mass fragments for deltamethrin are 181, 253, 77, 93, and 91. The characteristic peak for deltamethrin was found to be 284, respectively 285 for the protonated fragment M^+ . For the quantitative analysis it was calculated the cumulative peak area for both m/z fragments, 284 and 285, by mathematical integration within the limits 283.4 - 285.7 m/z. Based on known concentrations and calculated peak areas, it was constructed a calibration curve for deltamethrin. A similar approach was used for thiamethoxam solutions. The results (Table 1, graphically represented in Fig. 1) suggest that the adsorption experiments reached an adsorption plateau, after which continuing the adsorption process becomes inefficient.

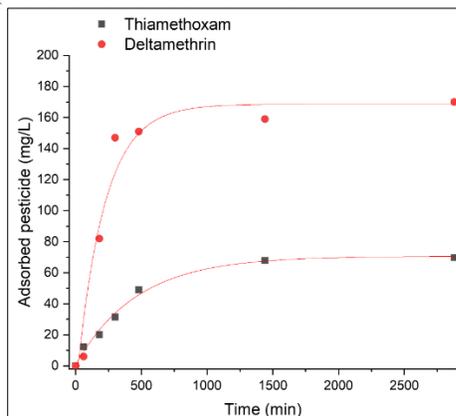


Fig. 1. Graphical representation of the adsorption process at different contact times

Table 1
 ADSORPTION OF SELECTED PESTICIDES AT DIFFERENT CONTACT TIMES (VALUES REPRESENTS
 PESTICIDES REMAINING IN THE SOLUTION AFTER DIFFERENT CONTACT TIMES)

Encoding	Contact time (hours)	Deltamethrin (mg/L)	Thiamethoxam (mg/L)
T ₀	0	200	200
T ₁	1	194.1	187.6
T ₂	3	118.2	179.8
T ₃	5	53	168.5
T ₄	8	48.9	151
T ₅	24	41	142.1
T ₆	48	30	130.2

The differences in adsorption (visible in Fig. 1) can be explained by the reduced affinity of the *nitro* group in the ionized form from thiamethoxam towards the carboxyl groups from chitosan.

The kinetic parameters are useful for the prediction of adsorption parameters, which are related with efficiency of adsorption. To determine the adsorption rate of thiamethoxam and deltamethrin on the prepared adsorbent three kinetic models such as Lagergren-first-order, pseudo-second-order kinetic models and intra-particle mass transfer diffusion model were applied in order to get insight on the adsorption process dynamics (a more detailed discussion regarding the kinetic models being previously presented [12]). The linear forms of these models were fitted based on the experimental data. Linear regression was used to determine the best fitting kinetic model, and the method of least squares is used for finding the parameters of the kinetic models (Fig. 2). The calculated kinetic constants and related coefficient of determination (R^2) are presented in Table 2.

Table 2
 VALUES OF THE KINETIC AND DIFFUSION PARAMETERS CHARACTERIZING PESTICIDE SORPTION
 ON THE USED ADSORBENT FOR THE THREE MODELS

Model	Parameter	Pollutant	
		Thiamethoxam	Deltamethrin
Pseudo-first order model	k_1 (min ⁻¹)	0.24834	0.11096
	q_{e1} (mg/g)	194.9552	80.78166
	q_{exp} (mg/g)	180.32	80.73
	R_{12}	0.9586	0.972
Pseudo-second order model	k_2 (g mg ⁻¹ min ⁻¹)	0.002685	0.001846
	q_{e2} (mg/g)	176.9912	78.80221
	q_{exp} (mg/g)	180.32	80.73
	R_{22}	0.99631	0.98972
Intraparticle diffusion model	k_{i1} (mg g ⁻¹ min ^{-0.5})	113.33	15.10
	k_{i2} (mg g ⁻¹ min ^{-0.5})	4.63	4.63
	C_1 (mg/g)	109.35	137.37
	C_2 (mg/g)	137.3728	34.12
	R_{i12}	0.99254	0.98135
	R_{i22}	0.91185	0.98424

From Figure 2 it was observed that the best fit to the experimental kinetic data and closest to the theoretical equilibrium values correspond to first order model. The first order model basically relies on the sorption capacity and the good concordance with experimental data suggesting that the adsorption mechanism might be a physisorption process. Regarding the intraparticle diffusion model, two stages can be observed in the adsorption process of pesticides on chitosan adsorbents. The high value of correlation coefficients for each stage show that intraparticle diffusion model favorably approximates the adsorption process. However, as the plots does not reach origin, it means that intraparticle diffusion is not the only rate-limiting step. The first stage of the plot (Fig. 2) is typically attributed to a fast-external surface adsorption. The second slower part shows a gradual adsorption stage due to intraparticle diffusion larger pesticide molecules and as a consequence of decreasing the concentration gradient. The whole behavior of the solid-pollutant system allows us to assume a combination of intraparticle diffusion and surface adsorption occurred simultaneously.

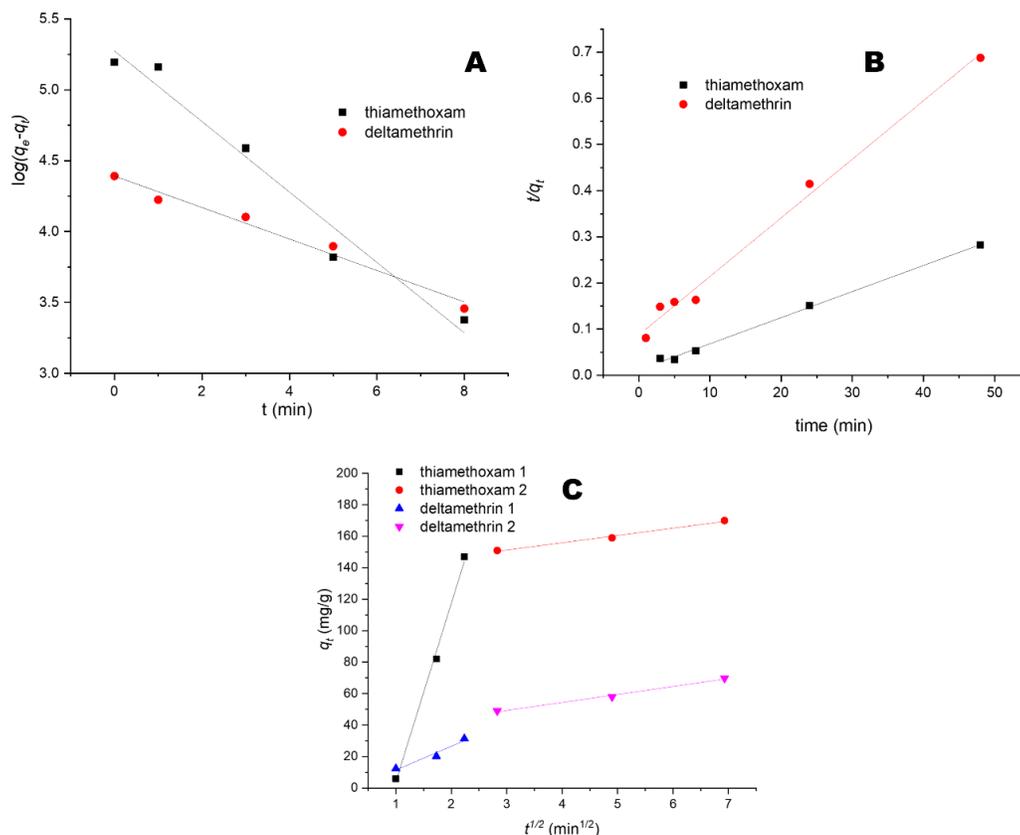


Fig. 2 Kinetic model of pesticide adsorption: a) pseudo-first order; b) pseudo-second order; c) intraparticle diffusion model

An *adsorption isotherm* provides a relationship between the solute concentration in the solution and the amount of pollutant adsorbed on the solid phase when the two phases are at equilibrium. The adsorption isotherm experimental data of pesticides were fitted by three common adsorption models: Langmuir, Freundlich and Sips (which is a combination of Langmuir and Freundlich) [12]. The theoretical parameters of adsorption isotherms along with regression coefficients (R^2) are presented in Table 3.

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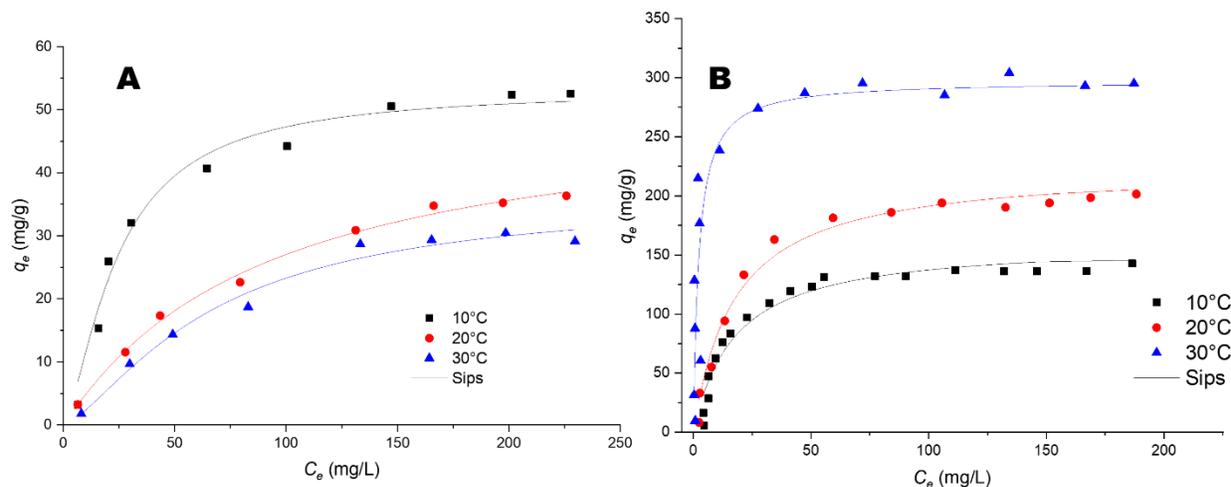


Fig. 3 Experimental data fitted according to Sips equation – influence of temperature on the adsorption process: a – thiamethoxam and b – deltamethrin.

The Langmuir parameters were used to assess the adsorption efficiency and affinity between the sorbate and sorbent using the separation factor (R_L):

$$R_L = \frac{1}{1+bc_0} \quad (3)$$

where C_0 (mg/L) represent the initial phenol concentration and b (L/mg) is the Langmuir constant.

The values of R_L at different temperature and initial concentrations for both pollutants fall between 0 and 1 (Table 4) which demonstrate that adsorption process is favorable especially at higher concentrations. Also, from the values of Freundlich isotherm parameter ($1/n$) which are below unity regardless the operating conditions it results a favorable adsorption.

Table 4
VALUES OF THE SEPARATION FACTOR AT DIFFERENT TEMPERATURES
FOR THE TWO PESTICIDES STUDIED

Pesticide/Temperature	10°C	20°C	30°C
Deltamethrin	0.79251	0.9012	0.74887
	0.80362	0.89028	0.89714
	0.73253	0.74166	0.43495
	0.731	0.62311	0.77104
	0.64852	0.50713	0.83956
	0.58394	0.39048	0.47482
	0.52546	0.27097	0.54198
	0.43365	0.20782	0.17489
	0.35099	0.17283	0.07888
	0.29745	0.14263	0.0474
Thiamethoxam	0.25755	0.12727	0.03171
	0.96973	0.98966	0.99091
	0.8308	0.93646	0.93106
	0.61255	0.77437	0.78508
	0.51214	0.68773	0.68932
	0.33175	0.5465	0.56788
	0.24178	0.4216	0.44995
	0.17869	0.36529	0.39743
0.13729	0.32656	0.3545	
0.12328	0.29759	0.32188	

Figure 3 shows the fitted equilibrium data for the Sips model which show the highest correlation coefficients (R^2) comparing with those of Langmuir and Freundlich models. This occur for both pesticides and for all working temperatures. In addition, the q_m value is 53.296 mg/g for thiamethoxam and 247.12 mg/g for deltamethrin. Obviously, the Sips isotherm, compared with the other two models was more suitable to describe the adsorption of pesticides on prepared adsorbents.

According to isotherm behavior it can be observed that in case of thiamethoxam adsorption process is exothermic in nature, while in the case of deltamethrin the process is endothermic since the pesticide amount on solid increase with temperature.

When comparing the maximum adsorption capacity determined for the developed material with literature data, it can be observed superior q_m values for deltamethrin. Hassan et al. [13] obtained a maximum value of 162.6 mg/g for the adsorption of deltamethrin on potassium hydroxide activated carbons prepared from pistachio nutshells (at 35°C), Al-Qodah et al. [14] obtained a value of 10.96 mg/g (at 25°C) for the adsorption on oil shale ash, while Ghafari et al. [15] registered values up to 41.7 mg/g for the adsorption on modified magnetic iron oxide nanoparticles. Regarding the adsorption of thiamethoxam, the experimental results also shows superior results, by comparison with literature data: Liu et al. [16] obtained an adsorption capacity of approx. 3 mg/g using magnetic graphene oxide- β -cyclodextrin, while Mir et al. [17] obtained a value of approx. 7.43 mg/g for the adsorption on TiO₂.

Effect of temperature on the adsorption of pesticides on prepared adsorbent

Adsorption isotherms obtained allow us to assess the effect of temperature on the adsorption process. It was found that higher temperature favored the adsorption of deltamethrin which suggests that the adsorption is endothermic in nature while for the thiamethoxam we observe an opposite behavior. The magnitude of thermodynamic parameters such as the changes in free energy (ΔG_0), enthalpy (ΔH_0), and entropy (ΔS_0) has been calculated with the help of van't Hoff plot using the following formulae:

$$\begin{aligned}\Delta G_0 &= \Delta H^0 + \Delta S^0 \\ \Delta G_0 &= -RT \ln K_d \\ \ln K_d &= \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}\end{aligned}$$

where R is gas constant (J/K mol), T is the absolute temperature (K) and K_d (L/g) is the adsorption equilibrium constant which is calculated by the ratio of amount of adsorbate adsorbed on unit mass of adsorbent to the amount remaining in the solution.

The adsorption equilibrium constant, K_c , for the binding of pesticides to prepared adsorbent surface were calculated from the slope of the q_e vs. C_e curve. The K_c values are expressed in L/g. In order to obtain a dimensionless parameter these values must be multiplied by water density (1000 g/L) [18]. Hence, by plotting $\ln K_c$ versus $1/T$ the values ΔS^0 and ΔH^0 can be obtained from the intercept and slope (Table 5).

Table 5
VARIATION OF THE STANDARD GIBBS FREE ENERGY, ENTHALPY AND ENTROPY CALCULATED

Pesticide	Temperature (°C)	ΔG_0 (kJ/mol)	ΔS^0 (kJ/mol)	ΔH^0 (kJ/mol)
Deltamethrin	10	21.73434	0.370891	83.11205
	20	21.45025	0.370891	83.11205
	30	29.21697	0.370891	83.11205
Thiamethoxam	10	16.73628	-0.15851	-61.5289
	20	13.56012	-0.15851	-61.5289
	30	13.59543	-0.15851	-61.5289

It is known that if ΔG_0 values goes up to -20 KJ gmol^{-1} , the process is in the range of physical adsorption while higher values of ΔG_0 fall in the chemical adsorption type of processes.

Moreover, ΔH^0 and ΔS^0 were obtained from the slope and intercept of Van-Hoff plots of $\ln K_c$ versus $1/T$ (Fig. 4) and the values are presented in Table 5. The negative enthalpy change (ΔH , kJ/mol) confirmed for thiamethoxam adsorption that in this case the removal is exothermic while in the case of deltamethrin the process is endothermic since ΔH have positive values.

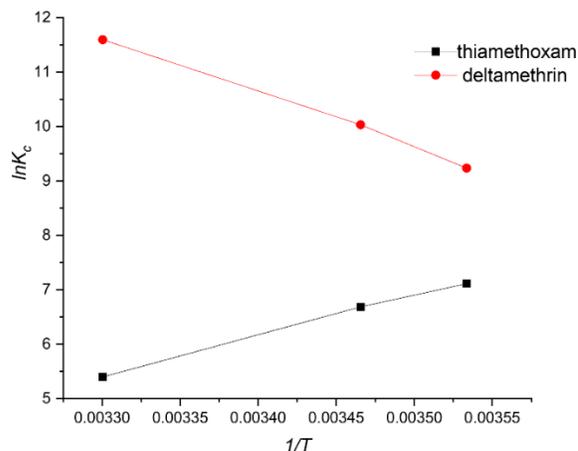


Fig. 4 Van't Hoff plot of $\ln K_c$ versus $1/T$

Conclusions

Previously presented magnetic composites were presented to be good adsorbents for the targeted pesticides. The Sips isotherm was found to be most adequate to describe the equilibrium process. Moreover, the adsorption experiments revealed that the used materials possess superior adsorption capacity when compared with literature data regarding the up-take of the selected active substances.

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