

Original Research

KINETIC AND THERMODYNAMIC ASPECTS OF PESTICIDE SORPTION ONTO
HORSE CHESTNUT SEED SORBENT

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Abstract

The sorbent obtained from horse chestnut acorn was tested for sorption capacity of acetamiprid in the aquatic media. Sorbent dose, contact time and temperature were varied. The kinetic data fitted best with a pseudo-first order model. Thermodynamic results indicate that the process of removing acetamiprid from the aquatic media was spontaneous at 25 °C. The maximum sorption capacity of the horse chestnut sorbent for acetamiprid ($q_{max}=13,52$ mg/g) was obtained with a sorbent dose 4 g/dm³, at 25 °C, pH 7.43, and initial concentration of acetamiprid 100 mg/dm³.

Keywords: biosorption, horse chestnut, *Aesculus hippocastanum*, acetamiprid.

INTRODUCTION

The intensive use of synthetic pesticides in modern agriculture has led to significant contamination of surface and groundwater systems, posing a severe threat to aquatic ecosystems and human health. Consequently, the development of efficient, low-cost, and sustainable remediation technologies is a global priority. Recent research has pivoted toward biosorption-utilizing waste biomass as a renewable alternative to expensive activated carbons [1]. Horse chestnut seed, a widely available but underutilized lignocellulosic byproduct, presents a promising matrix for this purpose. Its chemical composition, rich in starch, proteins, and polyphenols [2], provides a variety of functional groups that may serve as active sites for pesticide binding. This study aimed to investigate the feasibility of horse chestnut seed sorbent for removal of acetamiprid from aqueous solutions. In order to understand the underlying mechanisms governing this process, the analysis of kinetic models and thermodynamic parameters was performed to determine the rate limiting steps and to evaluate spontaneity and nature (physisorption, chemisorption or ion exchange) of the process.

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MATERIALS AND METHODS

The horse chestnut seeds were separated from the caps and left in a well-ventilated place to dry. The seeds were then ground in a rotary mill (SR 300, Retsch, Germany) and sieved granulometrically on a vibro device (AS 200 basic, Retsch, Germany). The fraction of 1 mm diameter was used for the experiments. The sorbent was not chemically or thermally modified.

In order to examine the influence of the sorbent dose on the biosorption of acetamiprid, a series of experiments was performed using 0.5, 1, 2, 4 i 6 g/dm³ of biosorbent. The initial concentration of 100 mg/dm³ of acetamiprid and the stirring rate of 100 rpm were constant. The pH of aqueous model solution of acetamiprid was 7.43 and was not adjusted after in order to observe the sorption process in natural conditions.

For thermodynamic parameters, 4 g of biosorbent was mixed with 100 cm³ of a 100 mg/dm³ solution of acetamiprid, at temperatures of 25 °C, 35 °C and 45 °C. For kinetic parameters, the experiments were conducted using 4 g of biosorbent at 25 °C and samples were taken after 5, 10, 20, 30, 40, 50 and 60 min. The suspensions were then filtered through cellulose 0.45 µm filters (Econofilters, Agilent Technologies, Germany) and the concentration of acetamiprid was determined in the obtained solutions.

RESULTS AND DISCUSSION

The amount of adsorbed acetamiprid onto horse chestnut seed biosorbent was calculated according to the Equation 1:

$$q_t = \frac{(c_0 - c_t)V}{m} \quad (1)$$

where c_0 and c_t represent the initial concentration and concentration of acetamiprid solution in time t (mg/dm³), respectively, V volume of acetamiprid solution (dm³), and m the mass of the biosorbent (g).

The effect of sorbent dose on acetamiprid removal from aqueous solution has been illustrated in the Figure 1.

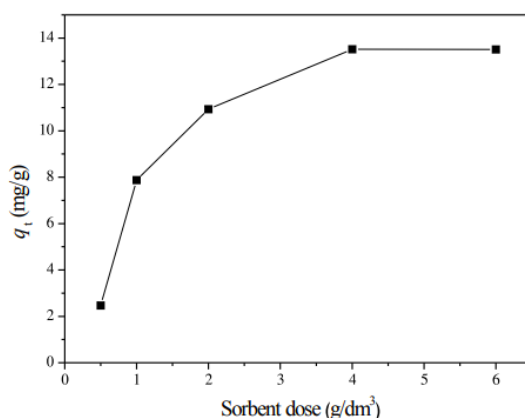


Figure 1 Effect of sorbent dose on acetamiprid removal from aqueous solution (pH=7.43, initial concentration of acetamiprid 100 mg/dm³, 25 °C, time 60 min)

The sorption capacity increased as the sorbent dose increased from 0.5 to 4 g/dm³, since larger number of binding sites was available for interaction with the molecules of acetamiprid. There was no significant increase in the sorption capacity when applying higher doses of sorbent. Therefore, the dose of 4 g/dm³ was used for further experiments.

The basic thermodynamic quantities, Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), are used to determine the spontaneity of a process, the nature of the reaction and the type of sorption and were calculated by using Equations 2 and 3:

$$\Delta G^\circ = -RT \ln K_c \quad (2)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (3)$$

Via linear plot of $\ln K_c$ vs. $1/T$, the values ΔH° and ΔS° were calculated (Figure 2).

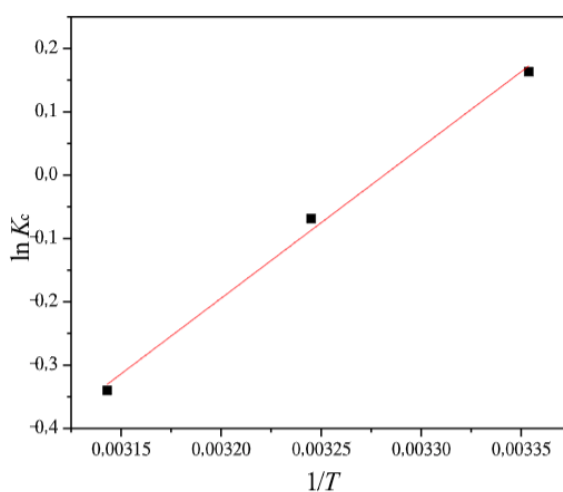


Figure 2 Thermodynamic dependence $\ln K_c = f(1/T)$ for the biosorption of acetamiprid onto horse chestnut seeds sorbent

According to results represented in the Table 1, the Gibbs free energy increases with an increase in temperature. The process is spontaneous at 25 °C ($\Delta G^\circ < 0$), which is not the case at higher temperatures ($\Delta G^\circ > 0$). The values of enthalpy and entropy show that biosorption of acetamiprid onto horse chestnut seed sorbent was exothermic, with the system becoming less disordered.

Table 1 Thermodynamic parameters of acetamiprid biosorption onto horse chestnut seeds sorbent

T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	R^2
298.16	-0.406	-19.829	-0.065	0.992
308.16	0.175			
318.16	0.899			

Based on ΔH° the mechanism of interaction between the sorbent and sorbate can be determined. Enthalpy value in the range of 2–20 kJ/mol indicates physical sorption, in the range of 20–80 kJ/mol indicates ion exchange, and the $\Delta H^\circ > 80$ kJ/mol indicates

chemisorption [3]. In this case, the most likely dominant mechanism of acetamiprid biosorption were physical interactions.

The sorption capacity increased up to 30 min of the sorption process, with no significant increase afterwards. Figure 3 shows the curves corresponding to the nonlinear forms of pseudo-first and pseudo-second order kinetic models. The kinetics of pollutant sorption from water to sorbents was described in the literature by pseudo-first and pseudo-second order models [4,5]. The nonlinear forms of the pseudo-first and pseudo-second order models are shown by equations 4 and 5:

$$q_t = q_e (1 - e^{-k_1 t}) \quad (4)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (5)$$

where k_1 (1/min) is the pseudo-first order rate constant, k_2 (g/mg min) is the pseudo-second-order rate constant, q_t (mg/g) is the sorbent capacity at time t , and q_e (mg/g) is the sorbent capacity in the equilibrium state.

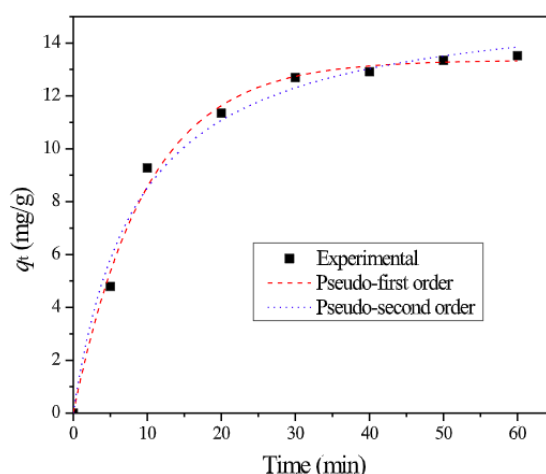


Figure 3 Kinetic models of pseudo-first and pseudo-second order of acetamiprid biosorption

Comparing the results of these two models, the pseudo-first order model is more adequate for describing the process of acetamiprid biosorption (Table 2).

Table 2 Kinetic parameters of sorption models of acetamiprid

Kinetic model	Parameter	Acetamiprid
Experimental	$q_{e,exp}$ (mg/g)	13.520
	$q_{e,cal}$ (mg/g)	13.354
Pseudo-first order	k_1 (1/min)	0.102
	R^2	0.993
Pseudo-second order	$q_{e,cal}$ (mg/g)	15.831
	$k_2 \times 10^3$ (g/mg min)	7.350
	R^2	0.986

The pseudo-first order model showed stronger correlation with the experimental data ($R^2 = 0.993$) compared to the pseudo-second order model ($R^2 = 0.986$). Also, the calculated value of sorption capacity according to the pseudo-first order model is closer to the experimental one.

CONCLUSION

According to obtained results, horse chestnut seeds could serve as effective and ecologically sustainable biosorbent for the removal of acetamiprid from polluted water. The kinetic analysis indicated that the data followed the pseudo-first order model more closely. Thermodynamic investigations confirmed the process to be exothermic ($\Delta H^\circ < 0$), spontaneous at 25 °C ($\Delta G^\circ < 0$) and characterized by decrease in randomness at the solid-solution interface.

REFERENCES

- [1] Danish, M., Ahmad, T. *Renew. Sustain. Energy Rev.* 2018, 87, 1–21.
- [2] Baraldi, C., Bodecchi, L., Cocchi, M., *et al.* *Food Chem.* 2007, 104(1), 229–236
- [3] Liu, Y., Liu, Y. J. *Sep. Purif. Technol.* 2008, 61, 229–242.
- [4] Lagergren, S., *Handlingar*, 1898, 24, 1–39.
- [5] Ho, Y.S., McKay, G. *Process Saf. Environ. Prot.* 1998, 76(4), 332–340.