PATELLIDAE SHELLS WASTE AS A BIOSORBENT FOR THE REMOVAL OF ALDRIN PESTICIDE FROM AQUEOUS SOLUTIONS

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Abstract

Adsorptive removal of aldrin insecticide from aqueous solutions by Treated Patellidae Shells (TPS) was investigated in a batch method under laboratory conditions. The effects of contact time, initial aldrin concentration, pH, ionic strength and temperature were studied. The kinetic analysis indicated that the pseudo-second-order model had the best fit to describe experimental data. Biosorption isotherms were also investigated using Freundlich, Temkin and Langmuir isotherm models. The experimental data fitted very well with Freundlich isotherm model. The maximum biosorption capacity was found to be 111.63 mg/g after 50 min of contact time, using 30 mg/L of pesticide and 25 mg of biosorbent. Thermodynamic data showed that the aldrin biosorption onto TPS was exothermic, spontaneous and highly favorable. The regeneration efficiency of spent TPS was studied using ethanol as a solvent. The TPS biosorbent showed good reusability characteristics and can be used as a highly effective, eco-friendly and low-cost adsorbent and an interesting alternative for removing pesticides from aqueous solutions.

Keywords: Patellidae shells, Adsorption, Aldrin, Insecticides, Wastewater, Reusability.

1. Introduction

The organochlorine pesticides (OCPs), which belong to the persistent organic pollutants group (POPs), were extensively used as insecticides from the 1950 until

Nomenclatures

a	Temkin isotherm constant, L/g
b	Temkin constant related to heat of biosorption, J/mg
C_0	Initial pesticide liquid phase concentration, mg/L
C_e	Pesticide liquid phase concentration at equilibrium, mg/L
k_1	Pseudo first-order kinetics equilibrium rate constant, min^{-1}
k_2	Pseudo second-order kinetics equilibrium rate constant, g/mg/min
K_c	Distribution coefficient
K_f	Freundlich constant, mg/L
K_L	Langmuir constant, L/mg
n	Biosorption intensity
pH	Hydrogen Potential
pH_{PZC}	Hydrogen Potential of the Zero Charge Point
q_e	Amount of equilibrium adsorption, mg/g
$q_{e, cal}$	Experimental equilibrium biosorption capacity, mg/g
$q_{e, exp}$	Calculated equilibrium biosorption capacity, mg/g
q_m	Maximum monolayer biosorption capacity, mg/g
q_t	Amount adsorbed at each time, mg/g
R^2	Correlation Coefficient
R	Universal gas constant, J/mol/K
R_L	Dimensionless separation factor
T	Temperature, K
t	Time, min
V	Solution volume, L
W	Biosorbent mass, g
$\varDelta G°$	Change in free energy, kJ/mol
$\varDelta H°$	Enthalpy, kJ/mol
$\varDelta S°$	Entropy, kJ/mol/K

Greek Symbols

θ	Bragg angle, deg.

Abbreviations

Conc	Concentration
ECD	Electron Capture Detector
EDS	Energy Dispersive X-ray Spectroscopy
FTIR	Fourier Transform Infra-Red
GC	Gas Chromatograph
OCPs	Organochlorine Pesticides
POPs	Persistent Organic Pollutants
Refs	References
SEM	Scanning Electron Microscopy
TPS	Treated Patellidae Shells
XRD	X-Ray Diffraction

1970 [1]. Among the OCPs, Chlorinated cyclodiene pesticides such as aldrin (1, 2, 3, 4, 10, 10-Hexachloro-1, 4, 4a, 5, 8, 8a-hexahydro-1, 4: 5, 8-dimethanonaphthalene) and dieldrin ((1aR, 2R, 2aS, 3S, 6R, 6aR, 7S, 7aS)-3, 4, 5,

6, 9, 9-hexachloro-1a, 2, 2a, 3, 6, 6a, 7, 7a-octahydro-2, 7: 3, 6-dimethanonaphtho [2, 3-b] oxirene), have a long history of use around the world. The production and usage of these highly persistent compounds were restricted in many advanced countries due to their high toxicity for human body and to their long persistence in the environment [2]. But after its restriction, some developed countries are still using them for agricultural and public purposes [3].

Several studies have indicated serious contamination of the water environment by these pesticides, including surface water [4] and groundwater [5]. Bioaccumulation through the consumption of food and the abiotic factors are the major routes of human exposure to aldrin and dieldrin [6]. Studies in animals show that both of them enter the body quickly after exposure. Once aldrin is inside the body, it quickly changes to dieldrin and then it stays in adipose tissue for a long time [1]. Dieldrin is more stable than aldrin and the other metabolites [7, 8]. High exposure to aldrin and dieldrin is reported to be carcinogenic and induces dysfunctions in the nervous, cardiovascular, endocrine and immune systems [6, 9].

The Stockholm convention on persistent organic pollutants (POPs) signed in 2001 by over 100 countries, pledged to stop the use of 12 POPs of biggest concern, including aldrin and dieldrin [10]. In the light of this convention, several countries have developed guidelines for aldrin and dieldrin. The U.S. Environmental Protection Agency has determined the oral reference dose to be 0.025 and 0.05 mg/kg/day for aldrin [11] and dieldrin [12], respectively, based on chronic dietary studies of aldrin and dieldrin in rats.

Numerous methods have been employed for the removal of OCPs from wastewater which includes advanced oxidation processes [13], ozonation [14] and adsorption [15]. Nevertheless, the adsorption is the most technology used [16]. Activated carbon was considered the most effective adsorbent [17], but its high cost led scientists to conduct studies to find other effective and low-cost adsorbents [18].

The purpose of this contribution is to study the efficacy of Treated Patellidae Shells on the removal of aldrin, which is an organochlorine pesticide widely used in Souss-Massa agriculture, from aqueous solutions. The widespread of this gastropod family in the coastal of Morocco, and its cheapness makes the TPS a new low cost and eco-friendly biosorbent. Biosorption studies were performed under various experimental factors such as biosorbent dose, contact time, initial pesticide concentration, temperature and *pH*. Various kinetic models such as pseudo-first-order and pseudo-second-order have been tested. Biosorption isotherms and thermodynamic studies have been investigated.

2. Materials and Methods

2.1. Chemicals

Technical grade aldrin of 99.9% purity and all other chemicals used in this study were supplied by Sigma Aldrich Company-Casablanca (Morocco). The aldrin is a Colorless solid with the following characteristics: The molecular formula is $C_{12}H_8Cl_6$; the solubility in water is 0.014 mg/L; the density is 1.60 g/mL; the melting point is 104.0°C and the molecular mass is 364.90 g/mol.

2.2. Preparation of treated patellidae shells (TPS)

The Patellidae Shells employed in this study were collected from the coast of the Massa city in Morocco. The shells were washed several times, treated with HCl acid 0.1 M for 10 min at room temperature, rinsed with distilled water and dried at 100°C for overnight. The shells were crushed and treated with NaOH 5% for 1h at room temperature. The resulting powder was rinsed with distilled water until neutrality and finally dried overnight at 60°C.

2.3. Experimental protocol

Biosorption tests were conducted in a set of Erlenmeyer flasks (150 mL) where 100 mL of aldrin solutions with initial concentrations of 10-40 mg/L were prepared. An amount of 25 mg of the TPS was added into each flask, covered with glass stopper and then, the flasks were placed on the shaker to reach equilibrium at constant temperature 22°C and with agitation speed of 120 rpm for 50 min as a contact time. After every 10 minutes, a flask is taken and filtered to obtain samples of 60 mL, which will then be preserved at 4°C. All samples were filtered before being analysed to minimize the interference of the carbon fines with the analysis. Each batch of the experiment was carried out in triplicate to get concordant results. Then, the aldrin was extracted from the aqueous solutions using the dichloromethane. The organic phase was dried by sodium sulfate and evaporated by a rotary evaporator. After that, a mixture of acetone-hexane was used to take the aldrin residues. The interfering substances were separated on silica columns. Finally, the purified extracts analysing were performed by gas chromatography (GC) with an electron capture detector (ECD). The amount of equilibrium adsorption q_e (mg/g) was calculated using the Eq. (1):

$$q_e = \frac{C_0 - C_e}{W} V \tag{1}$$

where C_0 and C_e (mg/L) are the aldrin liquid phase concentrations at initial and equilibrium adsorption, respectively. V is the solution volume (L) and W is the TPS mass (g). The % removal of aldrin is calculated by the Eq. (2):

$$\% \ Biosorption \ efficiency = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

2.4. Analytical procedures

Pesticide residues were analysed by Agilent 7890A gas chromatograph (GC), equipped with an electron capture detector (ECD) and an automatic liquid sampler. The capillary column type was RTX-50 (length = 30 m, internal diameter = 0.25 mm, film thickness = 0.25 µm). The GC oven program was as below: initial temperature was 70°C (maintained for 2 min) then increased firstly at 25°C/min to 150°C (maintained for 2 min), secondly at 3°C/min to 200°C (maintained for 5 min) and thirdly at 8°C/min to 280°C (maintained for 20 min). The injector temperature was 240°C and the detector temperature was 250°C. Helium was used as the carrier gas at a constant flow of 2 mL/min and nitrogen was used as make up gas at a constant flow of 70 mL/min. The injection technique was in the Splitless mode and the injection volume was 1 µL. GC calibration was reached from a curve obtained by the injection of standards at

three levels included in the linear range. The calibration line would be accepted if the correlation coefficient was $R^2 \geq 0.98$. The retention period of aldrin is 15.18 min. Figure 1 shows an Example of a chromatogram provided by the GC-ECD.
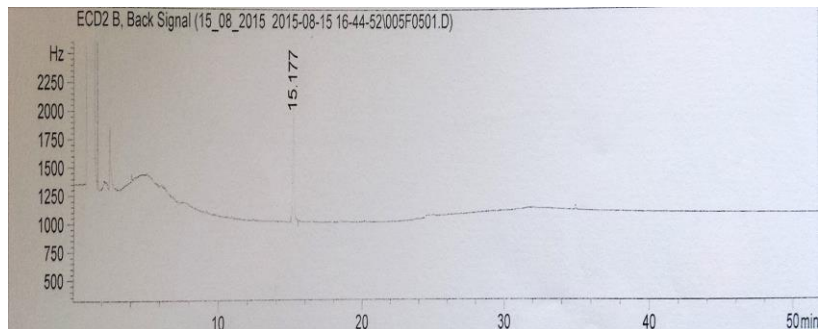

Fig. 1. Example of a chromatogram obtained by GC-ECD
(C_0 = 30 mg/L, W = 25 mg, V = 100 mL, at 22°C for 50 min).

3. Results and Discussion

3.1. Characterization of TPS adsorbent

The TPS biosorbent is identified by elemental analysis (PANalytical's WD-XRF spectrometers), scanning electron microscopy (FEI Quanta 200), X-ray diffraction (Philips X'Pert PRO), Infra-Red spectroscopy (ATI Mattson Genesis series FTIR UNICAM instrument) and by thermogravimetric differential thermal analysis (thermogram Shimadzu D60). The chemical composition of TPS reveals significant amounts of O (50.47%), Ca (32.41%) and C (15.83%) and small quantities of Na (0.5%) and Mg (0.79%) as shown in Fig. 2. The SEM analysis also presented in the Fig. 2, reveals the surface texture and porosity of biosorbent; it indicates the presence of fine particles, with regular morphology, having sizes between 1 and 3 μm. This regular and porous morphology can facilitate the diffusion and biosorption of aldrin molecules on TPS surface. The analysis by XRD depicted in Fig. 3 shows the presence of two phases in the TPS powder. The majority phase is the calcite, while the minority phase is the aragonite. The major peak is located at $2\theta = 29.47°$ (calcite), in addition to 23 other small peaks (calcite and aragonite). The XRD spectrum indicates the characteristic pattern of a single-phase, which is calcium carbonate $CaCO_3$. The Infrared spectra of the TPS are obtained by encapsulating 0.5 mg of the powder with 400 mg of KBr (0.1%) to get pastilles.

The FTIR spectrums given in Fig. 4, reveals the presence of three bonds before biosorption and four bonds after biosorption. The bonds at 712 cm^{-1}, 850 cm^{-1}, 1450 cm^{-1} and at 713 cm^{-1}, 849 cm^{-1}, 1452 cm^{-1} before and after biosorption respectively, are assigned to stretching and folding of the carbonate group (C=O and C–O) [19]. Similar results were found on biosorption of copper by Australian pine cones-based activated carbon [20]. The band at 798 cm^{-1} corresponds to C–Cl stretching mode according to Chen et al. [21]. This finding confirms the biosorption of aldrin molecules by TPS biosorbent. The TGA coupled to DTA was carried out from 22°C to 1000°C in air using 17 mg of TPS at a rate of 10°C/min (Fig. 5). The results of this study show that there are four losses. The first between 23 ° C and 115°C corresponds to the loss of water; it is equal to 1.9%. The second one between 115 °

C and 445°C (9.1%) corresponds to the loss of a part of organic matter. The third between 445 ° C and 610°C (3%) corresponds to the loss of the rest of organic matter, and the last loss, which is the most distinguished between 610°C and 825°C (37.4%) corresponding to the exhaust of the carbon dioxide [22, 23]. These results indicate that 87.9% of the TPS powder is composed of mineral matter, the majority of which is in the form of $CaCO_3$.
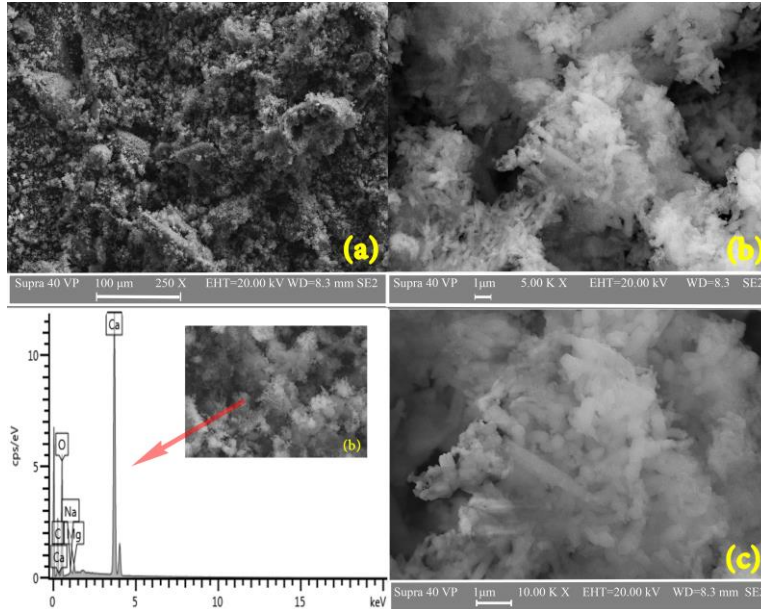

Fig. 2. SEM image and EDX of the TPS biosorbent:
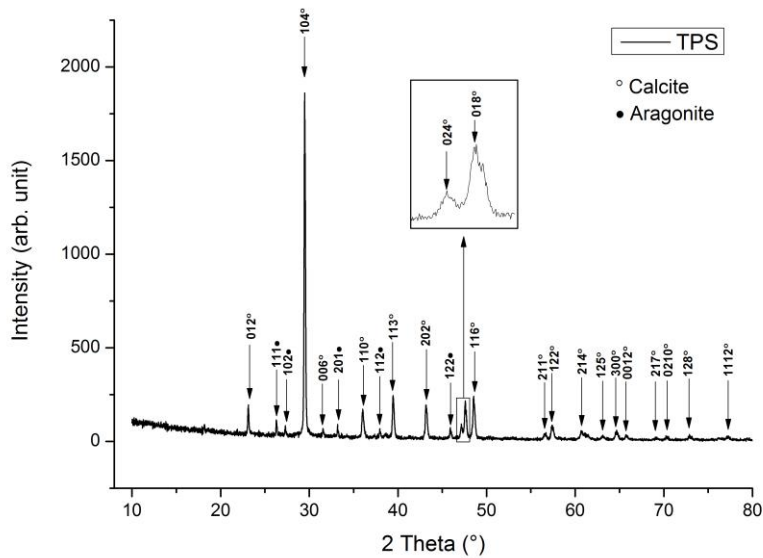**(a)×250, (b)×5000, (c)×10000.**
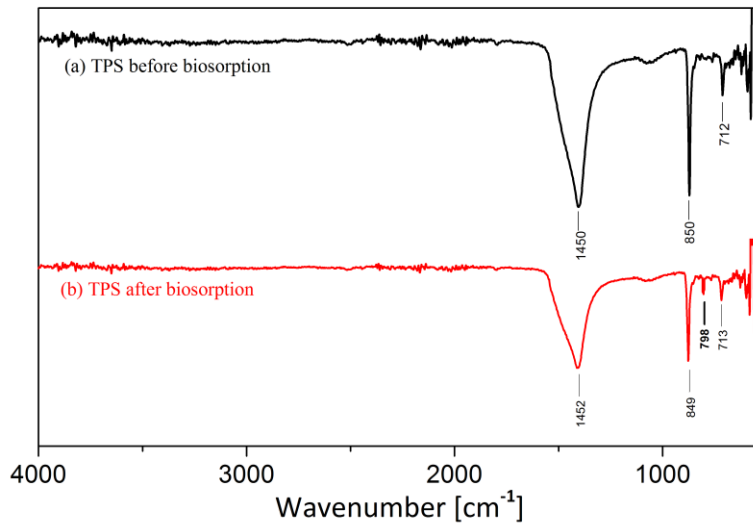

Fig. 3. X-ray diffraction of TPS.

Fig. 4. FTIR analysis of TPS: (a) before biosorption, (b) after biosorption.
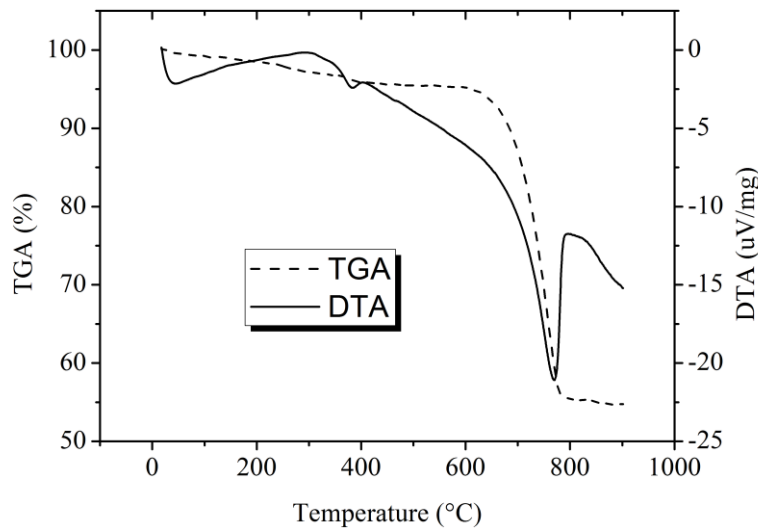

Fig. 5. DTA and TGA analysis (using 17 mg of TPS and at 10°C/min in air).

3.2. pH effect

The pH is one of the most important parameter that affects not only the surface charge of biosorbent, but also the charge of biosorbate molecules [24]. In this fact, the effect of initial pH on the biosorption capacity of aldrin pesticide onto TPS biosorbent was evaluated in pH range of 2-12 using 100 mL of 30 mg/L aldrin solutions at 22°C for 50 min. The pH is adjusted by adding solutions of NaOH and HCl 0.1M, and measured by a pH-meter model ISE HI3222 HANNA. Figure 6 illustrates the mean of the duplicated experimental results. These results

ensure that the pH considerably influences the biosorption process, especially under alkaline conditions. Figure 4 shows also that the amount adsorbed of aldrin decreases slightly from 93.29% (111.94 mg/L) to 92.52% (111.13 mg/L) with the increase of pH from 2 to 6 and then decreases sharply to 72.90% (87.48 mg/g) with increasing pH to 12. To explain these results, it's very important to determine the pH of the zero charge (pH_{PZC}) of the TPS. The curve of Fig. 4 shows also the variation of pH as a function of initial pH. The intersection of the curve with abscissa axis allows determining pH_{ZPC}, which is found equal to 8.4. For the pH values higher than 8.4, the TPS surface is negatively charged, while it is positively charged for pH less than 8.4. These results reveal that the uptake of aldrin onto TPS is highest in the acidic medium (A similar finding was shown on adsorption of arsenic (V) on TiO_2 [25]), which mean that the positive form of TPS is responsible for biosorption in this interval. It can be explained by the negative charge of aldrin that originates from the lone pairs of chlorine atoms. The weakest uptake at alkaline pH is due to electrostatic repulsive forces between the negative charge of TPS surface and the negatively charged pesticide molecules.
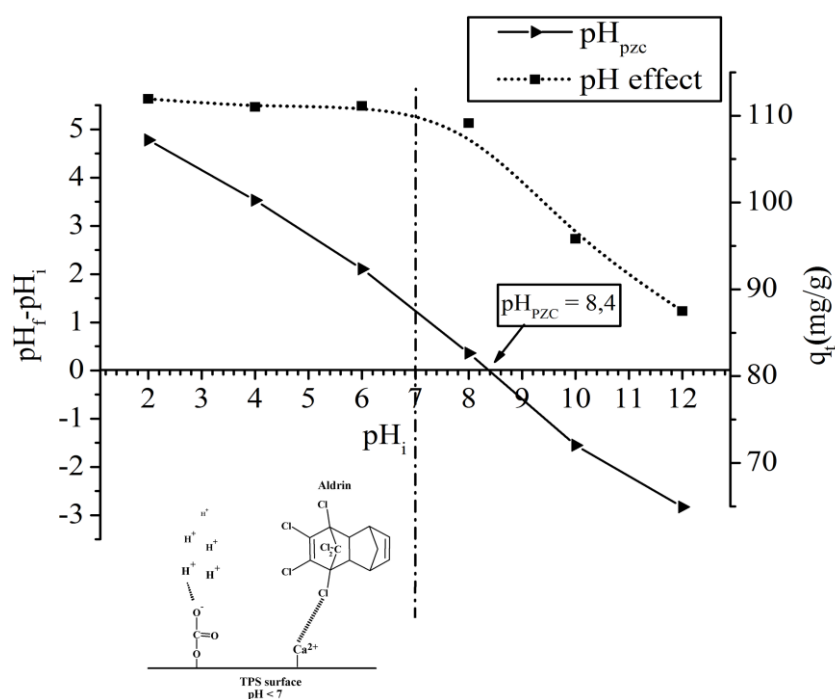

Fig. 6. Effect of pH on removal of aldrin onto TPS
(C_0 = 30 mg/L, W = 25 mg, V = 100 mL, at 22°C for 50 min).

3.3. Biosorbent dose effect

The effect of the biosorbent dose on the removal efficiency of aldrin pesticide from aqueous solutions onto TPS was determined by contacting different amounts of TPS in the range of 15-150 mg with 100 mL of 30 mg/L pesticide solutions at 22°C for 50 min and under constant agitation. Figure 7 shows the variation of TPS removal efficiency versus time. The percentage of aldrin removal was increased with increasing biosorbent dose and the optimum biosorption capacity

attained 91.72 % using 25 mg of TPS. This behavior is due to the increased number of sites available on the TPS biosorbent for pesticide biosorption. This phenomenon has already been observed in our previous work on the adsorption of carbaryl pesticide on treated eggshells [24]. For the following tests, we will use 25 mg of TPS per 100 mL of aldrin solution.
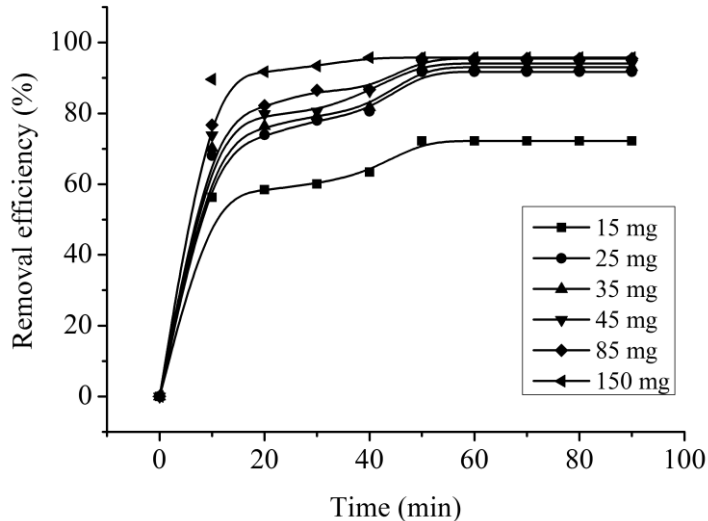

Fig. 7. Adsorbent dose effect on aldrin biosorption
(V = 100 mL, C_0 = 30 mg/L, at 22°C).

3.4. Initial concentration and contact time effects

To assess the effect of initial aldrin concentration and contact time on the adsorption uptake using TPS, different experiments were performed in the range of 10-40 mg/L as initial aldrin concentration and with 25 mg of TPS. Figure 8 depicts these results. The curves reveal that the amount of retained pesticide increases with increasing concentration. At high concentration, the ratio of the initial number of pesticide molecules to the available surface area is higher because the available sites become fewer, so the removal rate of pesticide depends upon concentration. However, at low concentration, the ratio is low. Consequently, the fractional biosorption becomes independent of initial concentration. The same finding was reveled on biosorption of Basic Fuchsin dye on the mussel shell biomass [26]. Figure 8 shows also that the amount adsorbed of pesticide increases with time for all initial concentrations. For the first 30 min, the biosorption uptake is rapid, then it proceeds at a slower adsorption rate and finally it attains saturation at 50 min. It appears that the initial concentration has no effect on the required time for equilibrium. Same result was obtained on adsorption of Cu (II) onto chemically activated areca catechu shells, while opposite finding has been described on biosorption of a basic dye on calcined eggshells [27, 28]. The high biosorption rate at the first stage was due to the uptake of aldrin by the exterior surface of the TPS biosorbent. However, when the exterior surface was saturated, the pesticide molecules penetrated into TPS pores and were biosorbed by the interior surface of the particles.
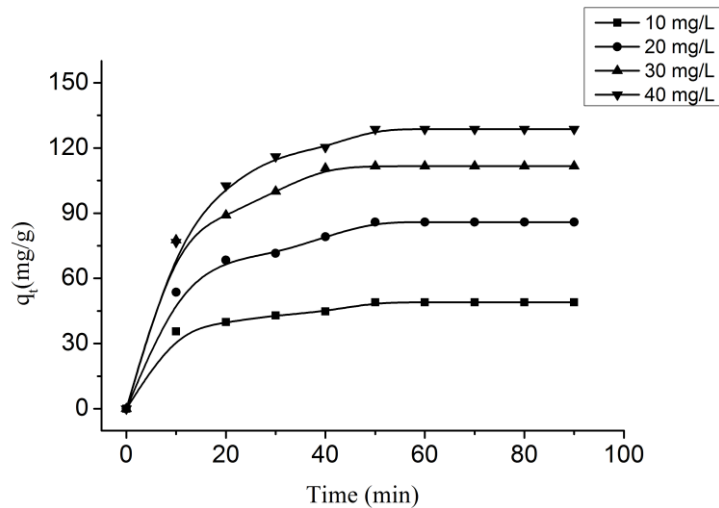
**Fig. 8. Initial concentration and contact time effects on aldrin
retention ($V = 100$ mL, $C_0 = $ (10-40) mg/L, $W = 25$ mg, $T = 22°C$).**

3.5. Ionic strength

Wastewaters often contain significant concentrations of salinity. Thus, it was
important to investigate the effect of salt in the aldrin biosorption. Figure 9
presents the effect of inorganic salt (NaCl) on biosorption of aldrin onto TPS
using 30 mg/L as pesticide concentration and 0.25 g/L of TPS under agitation at
22°C for 50 min. The curve shows that the adsorption rate decreases quickly from
91.36% (109.63 mg/g) to 75.70% (90.84 mg/g) with increasing NaCl
concentration from 0 to 6 mol/L and then decreases slowly to reach 74.68%
(89.62 mg/L) at 12 mol/L of NaCl. It is possible that the salt screens the surface
charge of biosorbent while competing with pesticide molecules. The same results
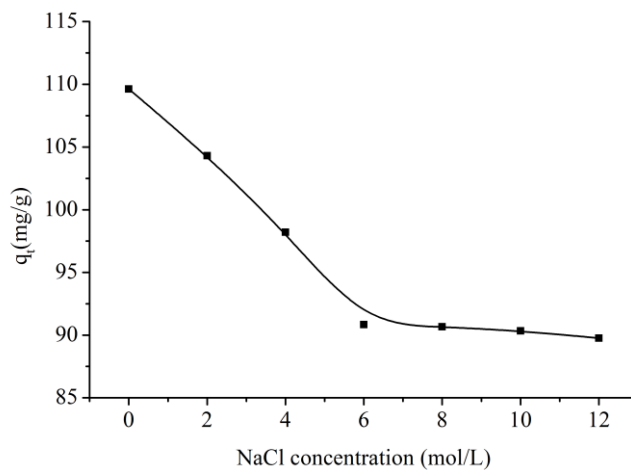were found for the adsorption of a cationic dye onto sepiolite [29].

**Fig. 9. Ionic strength effect on the aldrin biosorption on TPS ([NaCl] = 0-12
mol/L, $V = 100$ mL, $C_0 = 30$ mg/L, $W = 25$ mg, $T = 22°C$ for 50 min).**

3.6. Temperature effect

The adsorption of aldrin onto TPS was also evaluated as a function of temperature at 22, 35, 45 and 55°C using 30 mg/L of aldrin solution at pH 4 and 25 mg of biosorbent. The temperature is kept stable by means of a thermostated bath (JULABO CORIOC-BT5). Figure 10 shows that the decrease rate of biosorption is high from 91.97% (110.37 mg/g) to 83.36% (100.03 mg/g) with increasing temperature from 22 to 35°C, then this rate becomes low until 82.81% (99.38 mg/g) matching 60°C. These results suggest that the biosorption between TPS and aldrin pesticide is exothermic. This behavior can confirm that Van der Waals and dipole forces carry out the biosorption process. Moreover, the decrease of aldrin biosorption with increasing temperature can be explained by the increase of oscillation energy in the adsorbed molecules which favors their desorption [30].
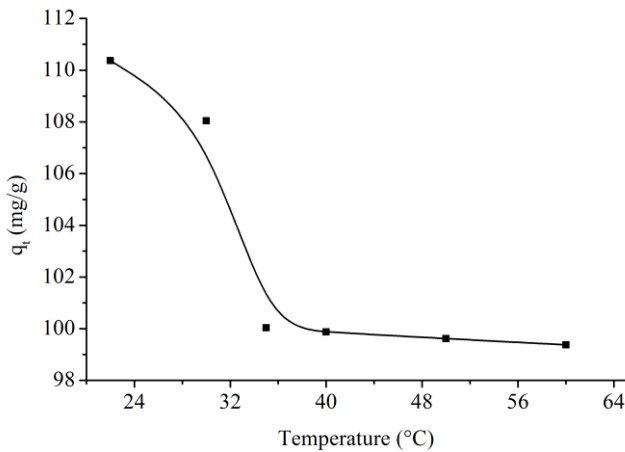

Fig. 10. Temperature effect on the aldrin biosorption onto TPS ($V = 100$ mL, $C_0 = 30$ mg/L, $W = 25$ mg for 50 min).

3.7. Kinetic studies

The biosorption rate constants were determined from the pseudo first order and the pseudo second order equations. For the pseudo first order, the integrated form of the Lagergren model [31] is written as shown in the Eq. (3):

$$Log\left(q_e - q_t\right) = Log\left(q_e\right) - \frac{k_1}{2.303}t \qquad (3)$$

where q_t is the amount adsorbed at each time (mg/g), and k_1 is the equilibrium rate constant of pseudo first order kinetics (min^{-1}) and t is time (min). k_1 and q_e are obtained by plotting the curve $log(q_e-q_t)$ versus t. Equation (4) depicts the linear form of the pseudo second order reaction [32]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (4)$$

where k_2 is the pseudo second order rate constant (g/mg/min). k_2 and q_e can be experimentally determined from the slope and intercept of the plot t/q_t versus t.

The parameters of the pseudo-first-order and pseudo-second-order models showed in Table 1 reveal good correlation coefficients R^2 for the pseudo-second-order model. In addition, the calculated values of the adsorbed amount ($q_{e,\,cal}$), which are in agreement with the experimental values of the adsorbed amount ($q_{e,\,exp}$), suggest that the adsorption of aldrin on TPS follows the pseudo-second-order kinetic model. The same results are found on sorption of cationic dye by wood of the jujube shell [33]. We can notice that the k_2 values decrease with increasing the initial concentration of aldrin, due to competition for biosorption sites at higher concentration.

Table 1. Kinetic parameters of aldrin biosorption on
TPS (V = 100 mL, C_0 = (10-40) mg/L, T = 22°C for 50 min).

Aldrin Conc. (mg/L)	$q_{e,\,exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1x10^3 (min^{-1})	$q_{e,\,cal}$ (mg/g)	R^2	k_2x10^3 (min^{-1})	$q_{e,\,cal}$ (mg/g)	R^2
10	38,94	25,57	13,29	0,8148	23,02	39,53	0,9999
20	75,92	29,79	74,35	0,8060	5,55	78,13	0,9997
30	111,63	32,78	237,36	0,8104	1,64	119,05	0,9979
40	139,62	34,87	580,36	0,8013	0,70	156,25	0,9947

3.8. Biosorption isotherms

Several isotherm models are employed to investigate the biosorption behavior. Among these models Langmuir, Freundlich and Temkin isotherms were used to find out which well explains the relationship between the biosorbent and the biosorbate. Langmuir isotherm [34] is a model for monolayer physisorption on homogeneous surface. The linear form of Langmuir equation is shown in Eq. (5):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{K_L}{q_m} \tag{5}$$

where K_L is the constant related to the free energy of biosorption and q_m is the maximum monolayer adsorption capacity (mg/g). The Freundlich isotherm is a model for multilayer biosorption on heterogeneous surface [35]. The linear form of Freundlich equation (Eq. (6)) is:

$$Log(q_e) = \frac{1}{n} Log(C_e) + Log(K_f) \tag{6}$$

where K_f and $1/n$ are the constants of the Freundlich model that indicate the relative biosorption capacity of the adsorbent (mg/L), and the intensity of the biosorption, respectively. The Temkin model assumes that the heat of biosorption decreases linearly with increasing coverage. The Temkin [36] linear form is given by the Eq. (7):

$$q_e = \frac{RT}{b} Ln(C_e) + \frac{RT}{b} Ln(a) \tag{7}$$

where *a* is the Temkin isotherm constant (L/g), *b* is the Temkin constant related to heat of biosorption (J/mg), *T* (K) is the solution temperature and *R* (= 8.314 J/mol.K) is the universal gas constant.

Table 2 presents all the constants and correlation coefficients R^2 values obtained from the application of the three models for the biosorption of aldrin onto TPS. The examination of these parameters show that R^2 obtained from the Freundlich isotherm model ($R^2 = 0.9952$ at 22°C) were higher in comparison with Langmuir and Temkin models. These results prove that the Freundlich model is more suitable to describe the adsorption of aldrin on TPS biosorbent. In addition, the value of $n_f > 1$ implies that biosorption is favorable and of a physisorption nature.

Table 2. Isotherm parameters for the aldrin uptake on TPS
($C_0 = 30$ mg/L, $W = 25$ mg, $V = 100$ mL, $T° = 22$-$55°C$ for 50 min).

Isotherms		Temperature			
		22°C	35°C	45°C	55°C
Langmuir	R^2	0.9817	0.9929	0.9956	0.9961
	q_m	166.67	188.68	189.04	208.33
	K_L	1.0333	2.4340	3.2136	4.7500
Freundlich	R^2	0.9952	0.9947	0.9956	0.9961
	K_f	73.30	53.46	45.48	38.22
	n_f	2.2568	1.8352	1.7572	1.6116
Temkin	R^2	0.9872	0.9905	0.9936	0.9961
	a	10.732	4.276	3.010	2.167
	b	70.667	63.872	62.698	60.819

3.9. Biosorption thermodynamic

Thermodynamic parameters such as the change in free energy $\Delta G°$ (kJ/mol), entropy $\Delta S°$ (kJ/K/mol) and enthalpy $\Delta H°$ (kJ/mol) reflect the favorability of biosorption and allow distinguishing between physical and chemical adsorption [37]. The value of $\Delta G°$ is calculated using the Eq. (8), while the $\Delta H°$ and $\Delta S°$ values are found using the Eq. (9):

$$\Delta G° = -RT \times Ln(K_c) \tag{8}$$

$$Ln(K_c) = -\frac{\Delta H°}{R} \times \frac{1}{T} + \frac{\Delta S°}{R} \tag{9}$$

where K_c is the distribution coefficient ($K_c = q_e/C_e$)

Thermodynamic data were determined and presented in Table 3. The $\Delta H°$ and $\Delta S°$ values were obtained from the slope and intercept of Van't Hoff plots. The negative value of $\Delta S°$ shows the decreased disorder and randomness at the solid solution interface. The negative value of the enthalpy change $\Delta H°$ indicates that the biosorption was exothermic. The value of $\Delta G°$ within the range of 0-20 kJ/mol suggests that the dominant mechanism was the physisorption [38]. The negative values of $\Delta G°$ show that the biosorption of aldrin onto TPS was highly favorable and spontaneous [39]. $\Delta G°$ decreased as the temperature increased,

indicating a higher driving force and therefore increased the uptake capacity. Similar findings have been reported for adsorption of 2,4-dichlorophenoxyacetic acid on granular activated carbon [40].

Table 3. Thermodynamic parameters of aldrin retention onto TPS (T = 22-60°C, C_0 = 30 mg/L, W = 25 mg, V = 100 mL).

Temperature (K)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/mol/K)
22	-5,981	-23,529	-0,061
30	-5,545		
35	-4,127		
40	-4,168		
323	-3,836		
333	-3,808		

3.10.   Regeneration of TPS

The environmental applications of TPS biosorbent depend upon its capacity to be regenerated. Therefore, the TPS reuse was investigated using ethanol as a regenerant solvent. Batch equilibrium tests were performed on the fresh TPS using 100 mL of 30 mg/L aldrin concentration and 25 mg of TPS, at 30°C and under agitation of 120 rpm for 50 min. The TPS was separated from the solution, washed and dried at 110°C. The aldrin was next desorbed by 100 mL of ethanol 60 % at the same conditions of biosorption tests and the pesticide residual dose in the solution was measured. The spent biosorbent was finally calcinated at 400°C for 30 min for the reactivation. The change in uptake biosorption as a function of cycle number is presented in Fig. 11. The uptake capacity decreases from 91.36 % (109.63 mg/g) to 85.89 % (103.07 mg/g) going from the first to the fifth cycle respectively. Close findings were obtained after three cycles for the adsorption of carbofuran on banana stalks activated carbon [41]. These results indicate that the TPS has good reusability characteristics for the biosorption of aldrin and can be used as an alternative to the commercial adsorbents.
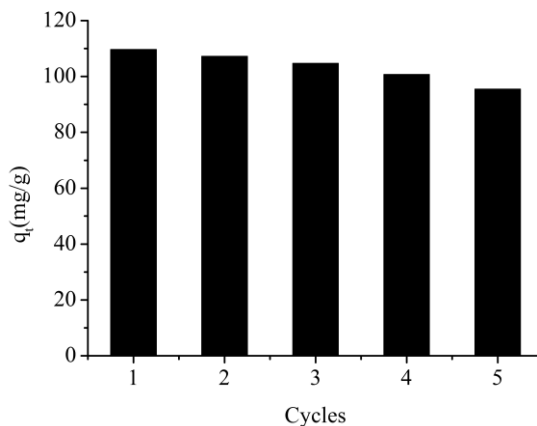

Fig. 11. Regeneration cycle effect on the TPS biosorption (C_0 = 30 mg/L, W = 25 mg, V = 100 mL, T = 22°C, *Solvent* = ethanol 60% for 50 min).

3.11. Comparison between some biosorbents to remove pesticides

The biosorption efficiency values of various biosorbents are depicted in the Table 4. These results show that TPS biosorbent can be ranked among the most effective biosorbents studied to date, with an adsorption capacity of 111.63 mg/g.

Table 4. Effectiveness of some adsorbents to eliminate pesticides from aqueous solutions (Current study: V = 100 mL, C_0 = 30 mg/L, W = 25 mg, T = 22°C, *Solvent* = ethanol 60%).

Biosorbents	Pesticides	Kinetic model	q_{max} (mg/g)	Refs
Olive Stone	Aldrin	Pseudo-second-order	0.0195	[42]
Neutralized Red Mud	Aldrin	Pseudo-second-order	0.15514	[43]
Treated Patellidae Shells (TPS)	Aldrin	Pseudo-second-order	111.63	Current study

4. Conclusion

The biosorption behaviour of aldrin onto Treated Patellidae Shells was investigated in the batch experiments. The biosorption was found to be dependent on pH, initial aldrin concentration, biosorbent dose, contact time, ionic strength and temperature. In comparison with many supports, the equilibrium rate of biosorption was quite fast with a value of 50 min. The presence of the functional groups allows a good surface adsorption of aldrin onto TPS at acid conditions. The biosorption mechanism was found to be physisorption. The pseudo-second-order kinetic model and the Freundlich isotherm best represented the equilibrium data. Thermodynamic study was indicating that the biosorption was exothermic, spontaneous and highly favorable. These results show that the TPS has a very good reusability performance and can be employed as alternative for wastewater treatment.

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