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Study of two cork species as natural biosorbents for five selected pesticides in water

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Abstract

The present study evaluates biosorption efficiencies of pesticides atrazine, fluazifop-P-butyl, lactofen, lambda-cyhalothrin and chloropyrifos on corks of *Quercus cerris* and *Quercus suber* trees. The studies were carried out in batch and effects of pH (3, 7 and 9), temperature (10, 20, 30 and 40 °C), and time on adsorption were measured. Pesticide analyzes were performed with an Ion-trap Mass Spectrometer following the SANCO/10232/2006 EU extraction protocol for pesticides. The results show that the highest adsorption efficiency (80% and 70%) of the pesticides was found at pH 3, 30 °C and 360 minutes. The adsorption kinetics of pesticides followed pseudo-second order and pseudo-first order kinetics. The results obtained in this study show that *Q. cerris* and *Q. suber* corks can be used to develop efficient and economical cork-based alternatives for the treatment of environments contaminated with pesticides.

Keywords: Biochemistry, Chemistry, Chemical engineering, Organic chemistry, Environmental science, Biotechnology

1. Introduction

In the last decades, the intensive use of pesticides has motivated controversial discussions on environmental issues of great relevance such as the quality of surface water and groundwater. The water resources contamination with these pollutants can derive from their application in agricultural areas, accidental spillage as well as by the effluent treatment processes that are still inefficient to remove these pollutants (Aguiar et al., 2014).

Pesticides can threaten sensitive species and cause dysfunctions in the reproductive capacity. They are also a danger to humans by reaching the population through food and drinking water e.g. exposure to neurotoxic pesticides may increase the risk of Parkinson's disease (Wang et al., 2011). Some pesticides are not toxic even at high concentration but they may show synergistic toxicity in the presence of other pesticides such as the case of atrazine and chloropyrifos (Belden and Lydy, 2000). European Union Directive 80/777/EEC sets the maximum allowable concentration of individual pesticides as 0.1 μg/L and total amount of pesticides as 0.5 μg/L in natural mineral water.

In agricultural production, large quantities of pesticides end up contaminating soil, water, air and living beings. In the environment, the organic compounds are degraded by natural microorganisms but certain pesticides are extremely recalcitrant to biological degradation, a fact which explains the increased lifetime of these compounds (Olivella et al., 2012). A number of alternatives can be used to remove pesticides from wastewater. Among the most used processes are the application of clays (Cruz-Guzmán et al., 2005) or activated carbon (Bacaoui et al., 2002) which show positive results, although a great difficulty, especially in the case of activated carbon, is the cost. In the last decades, technologies that use natural biosorbent materials have gained importance as effective and low cost alternatives for the treatment of contaminated water (Bhatnagar et al., 2010). In this way, studies related to biosorption processes have increased, as shown by the high number of published works (Ho et al., 2000; Juhasz et al., 2002; Gadd, 2009).

Pollard et al. (1992) suggested the use of biosorbents from biomass, including industrial byproducts. Several low-cost alternative materials such as chitosan fibers, resins, wood chips, chip chips, coconut shells were studied to replace activated carbon for the sorption of different pollutants such as pesticides and other compounds (Domingues et al., 2005; Şen et al., 2015).

Biosorbents can be interesting solutions for the removal of pesticides due to their physical and chemical affinity. External factors such as pH, temperature, the possible presence of nutrients and other metals influence the mechanism of adsorption and, consequently, the process efficiency and selectivity (Şen et al., 2015). Studying

the physical-chemical interactions between the molecules of pesticides and biosorbents can provide important information to understand the dynamics of the retention processes and their transport in the environment.

In addition, biosorbents can be used to generate important, low-cost technologies for contaminated water treatment systems (Aksu, 2005; Villaescusa et al., 2004; Gadd, 2009). The low costs are related to their availability, involving only transport costs and few raw material process costs.

In this context, biosorbents based on the tree barks were studied (Villaescusa et al., 2002). The cork of some species, namely of *Quercus suber* and *Quercus cerris* can be used for adsorption of pesticides. Investigations on the biosorption of Cr(VI) by *Q. cerris* and *Q. suber* corks have shown that these species have similar chemical and anatomical characteristics as well as high heavy metals adsorption capacities which suggests the application of both corks in different adsorption process (Şen et al., 2012). The cork has unique anatomical and chemical properties, and it is a valuable industrial raw material with numerous application possibilities, the most important the production of stoppers (Pereira, 2007). Cork has properties that may be of interest for wastewater treatment, such as low density and buoyancy. Recently, the cork adsorption approach has gained importance after application of cork as an adsorption substrate for the removal of pollutants. This potential is associated with the important binding sites present in cork, as well as the adsorption capacity (Şen et al., 2015; Chubar et al., 2004).

The present study is in line with the growing demand for information on pesticide removal with the use of natural sorbents. The objective of this work is to study the efficiency of the removal of pesticides in water using corks from *Q. cerris* and *Q. suber* outer barks and to evaluate the influence of the adsorption conditions of pH, temperature and contact time. Five largely used pesticides are tested: atrazine, fluazifop-P-butyl, lactofen, lambda-cyhalothrin and chlorpyrifos.

2. Materials and methods

2.1. Characteristics of the studied pesticides and biosorbents

For the present biosorption study the following pesticides were selected: atrazine, fluazifop-P-butyl, lactofen, lambda-cyhalothrin and chlorpyrifos, with a purity of 99% obtained from Sigma-Aldrich (Missouri, USA). These pesticides were chosen because they are commonly used in the corn and soybean crops worldwide. The chemical structure of these pesticides is presented in Fig. 1, and Table 1 summarizes their physicochemical properties.

Two cork biosorbents were used: a) triturated reproduction cork from *Quercus suber* (250−420 μm) b) cork fractionated from *Quercus cerris* outer bark (250−420 μm).
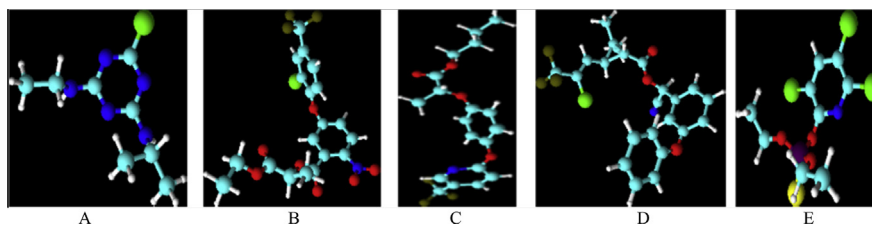
Fig. 1. Chemical structure of the studied compounds: Atrazine (A), Lactofen (B), Fluazifop-P-butyl (C), Lambda-Cyhalothrin (D) Chloropyrifos (E).

Table 1. Physical and chemical properties of the pesticides studied. Sw - Solubility in water at 20 °C; K_{ow} - partition coefficient octanol-water; K_{oc} - adsorption coefficient in soil organic matter; DT_{50} — soil degradation half-life (aqueous hydrolysis at 20 °C and pH 7); GUS — Leaching potential (Groundwater Ubiquity Score) (Aguiar et al., 2015).

Pesticide	Type	Formula	S_w (mg L^{-1})	Log K_{ow}	K_{oc} (mL g^{-1})	DT_{50} (days)	Gus
Atrazine	Herb.	$C_8H_{14}ClN_5$	35	2.7	100	86	3.30
Fluazifop-P-butyl	Herb.	$C_{19}H_{20}F_3NO_4$	0.93	4.5	3394	78	0.00
Lactofen	Herb.	$C_{19}H_{15}ClF_3NO_7$	0.5	-	10000	-	0.00
Lambda-cyhalothrin	Insect.	$C_{23}H_{19}ClF_3NO_3$	0.005	5.5	283707	Stable	-3.28
Chlorpyrifos	Insect.	$C_9H_{11}Cl_3NO_3PS$	1.05	4.7	5509	53	3.63

A detailed information on the chemical compositions of these materials can be found elsewhere (Şen et al., 2010).

2.2. Effect of pH and time on adsorption

The tests used a pesticides concentration of 10 μg L^{-1} in 1 L of purified water (Millipore, Bedford, MA) using 134 (67 for each cork adsorbent) shakers maintained at 22 °C ($\pm$2 °C). The pH of the water was adjusted to 3, 7 and 9 to test for pH differences. A total of 4 g of cork granules were added to each solution and the shakers were covered with aluminum foil to avoid photo degradation of the pesticides. The shakers were placed on a shaking table for 30, 60, 120, 240, 360, 720 and 1440 minutes, at the end of each time the samples were analyzed in two repetitions.

2.3. Effect of temperature on adsorption

The previous tests showed that pH 3 and 360 min are the best conditions for the adsorption. The influence of adsorption temperature was studied by keeping these pH and time conditions, and changing only the temperature. Four temperatures were tested by heating in a shaking incubator: 10, 20, 30 and 40 °C. The equipment temperature error was $\pm$0.5 °C. Two repetition tests were carried.

2.4. Adsorption kinetics

In order to evaluate the adsorption rate of the pesticides onto the corks, the previously determined adsorption values at different time intervals were used. Since pseudo-first-order and pseudo-second-order models are frequently applied for kinetic analysis of organic compounds, these models were selected in the current study to explain the adsorption kinetics of corks.

Pseudo-first order kinetic models are defined as following:

$$\ln\left(\frac{X}{X-x}\right) = k1.t$$

where X and x are adsorption capacities (mg/g), k1 is the first-order rate constant for the pseudo-first-order model and t is the time (Ho, 2006).

Pseudo-second-order kinetic models are defined as the following equation:

$$\frac{t}{qt} = \frac{1}{k2qe^2} + \frac{1}{qe}.t$$

where qt and qe are the amount of adsorbed material (mg/g), k2 is the second-order rate constant and t is the time (Ho, 2006).

2.5. Ion-trap mass spectrometry

The pesticides atrazine, fluazifop-P-butyl, lactofen, lambda-cyhalothrin and chlorpyrifos pesticides were used, with a purity of 99% obtained from Sigma-Aldrich (Missouri, USA). The solutions (10 mg/ml) and the dilutions (0.001, 0.01, 0.1, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 40 and 50 μl) were prepared in ethyl acetate to perform the calibration curve. Standards and solutions were maintained at -4 °C. Ethyl acetate, methanol and water solvents were chromatography grade from Merck (Darmstadt, Germany). Atrazine-D5, 99% pure from Supelco (Bellefonte, PA, USA) was used as a substitute standard.

The extraction protocol was elaborated according to SANCO/10232/2006 UE (European Commission, 2006). For extraction of the pesticides C18 cartridges were used. Prior to extraction 0.1 μl of Atrazine-D5 was added to the 1 L sample as a replacement standard. The samples were filtered using 0.45 μm and 47 mm diameter porosity cellulose membrane from Merck Millipore (Darmstadt, Germany).

A 1 L volume of the water sample was extracted using SPE solid phase extraction cartridge C18 (Milford, MA, USA) (Fig. 2). The cartridges were first cleaned with 6 mL of ethyl acetate, later with 6 mL of methanol and 6 mL of purified water (Millipore, Bedford, MA). The samples were then percolated through a vacuum system from JT Baker (Phillipsburg, NJ, USA) at a flow rate of 6 mL/min.
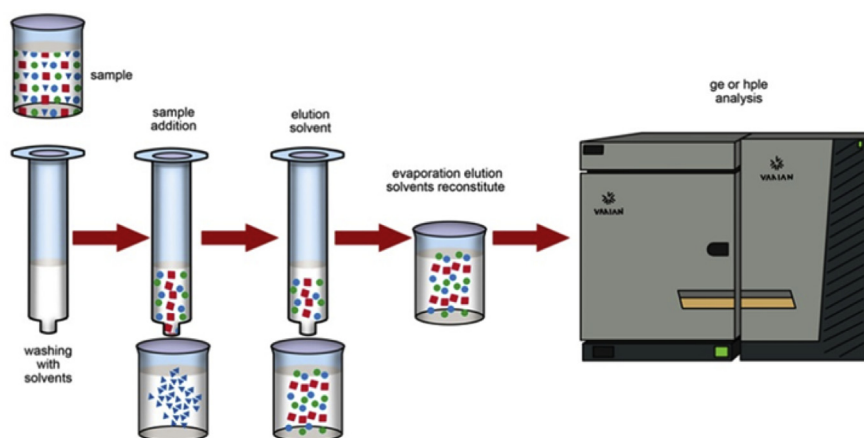
Fig. 2. Extraction of pesticides by the SPE method.

Thereafter, the cartridges were dried under vacuum for 15 minutes to remove water and then extracted with 6 mL of ethyl acetate and 6 mL of methanol. The 12 ml volume was transferred to a vial (Agilent Technologies, USA) and evaporated in a 40 °C Dry Block (Marconi, SP, BRA) with a mild nitrogen stream from White Martins (Praxair Technology Inc., USA) to near dryness and reconstituted to 100 μL of ethyl acetate, then passed into the vortex and transferred to a vial. Then 1 μl was injected into a gas chromatograph coupled to a mass spectrometer (GC-MS).

GC-MS analysis was performed using a Varian 431-GC gas chromatograph coupled to Varian 220 MS ion trap mass spectrometer equipped with a capillary column VF-5ms (30 m × 0.25 mm, 25-μm film thickness. The GC oven was programmed from 90 °C, hold 0.5 min, to 160 °C (hold 4 min) at 15 °C min^{-1}, then to 280 °C (hold 10 min) at 20 °C min^{-1}. The GC interface and ion sources were 280 and 200 °C, respectively. The ion trap mass spectrometer was operated in electron impact ionization with ionization energy of 70 eV and emission current of 300 mA. Helium at a constant flow of 1.0 mL min^{-1} was used as the carrier gas. The injection volume was 1 μL in a splitless mode (1 min) with injector temperature at 250 °C.

From the collision induced dissociation (MS/MS), three mass fragment ions were selected for each compound: atrazine (m/z 122*, 132 and 200), chlorpyrifos (m/z 258*, 286 and 314), fluazifop-P-butyl (m/z 254, 238* and 282), lambda-cyhalothrin (m/z 152*, 154 and 181), and lactofen (m/z 223*, 300 and 344), with the major mass fragment ions used as precursor ion. The marked mass fragment ions were used for quantification analysis, and the other two were used for structural confirmation.

The stock solutions were prepared for all agrochemicals (99 % purity, Sigma-Aldrich, Missouri, USA) at 10 mg mL^{-1} in ethyl acetate and were kept in −4 °C. Atrazine-D5 was checked using the following ions m/z 127*, 139, and 205. A calibration curve with diluted standards was performed in 0.01−30 μg L^{-1}. Calibration

curves resulted in correlation coefficients of 0.99 and relative standard deviation less than 9 % (n = 4) for all compounds. The lower quantification point was 0.01 µg L^{-1}.

The methods of analysis are in accordance with SANCO/10232/2006 EU by European Commission (2006). The identification and confirmation of the target compounds were performed according to the criteria: (I) deviation of the retention time against a standard of less than 2s, (II) three m/z characteristic per compound (except the substitution pattern that had 2 m/z) and (iii) the intensity of the m/z characteristic with respect to the m/z of the standard: no more than 15% of variation (Table 2).

2.6. Statistical analysis

The statistical significance of the different samples was tested by analysis of variance (ANOVA) with probability of $p < 0.05$. The means were compared using the Tukey test. Correlation tests were performed to determine which equilibrium time, pH and temperature are ideal for corks of *Q. suber* and the *Q. cerris*. They were determined at the 5% confidence level. The software used was R version 3.5.2.

To calculate the percentage of pesticide removal, several values of time, pH and temperature were used, as referred in the sub-sections above. The percentage of removal was calculated by the difference between the final and the initial values. In the drawing of the removal efficiency graphs, standard deviation analyzes were included through the error bars.

3. Results and discussion

3.1. Effect of pH and time

The protonation potential along with the adsorption temperature and time are the most important parameters of the adsorption system (Şen et al., 2012). Therefore, the adsorption tests were carried out with the pH variation of the sample between

Table 2. Quantification parameters obtained for GC-MS, and ions used for quantification (m/z1) and identification.

Component	Range	R^2	Recovery (%)	m/z1 m/z2 m/z3	LQ*
Atrazine	0.01−50 µg/mL	0.990	97	200-132-122	0.01
Chlorpyrifos	0.01−50 µg/mL	0.998	98	314-286-258	0.01
Fluazifop-P-butyl	0.01−50 µg/mL	0.991	97	282-254-238	0.01
Lactofen	0.01−50 µg/mL	0.995	89	344-300-223	0.01
Lambda-cyhalothrin	0.01−50 µg/mL	0.996	90	181-154-152	0.01

*Limit of quantification (µg/mL).

acid, alkaline and neutral values (pH 3, pH 7 and pH 9). Also adsorption equilibration time was calculated.

Significant differences were found between the different pH values of the samples ($p < 0.05$) and pH 3 was found as ideal for these biosorbents. However, there was no statistical difference ($p > 0.05$) between the two types of cork, demonstrating that both behaved in the same way in different pH values. The effect of pH on the sorption of different pesticides by *Q. suber* cork is shown in Fig. 3.

By altering contact time and pH of the samples for each pesticide, it was possible to identify how pH and contact time affect the removal efficiency of the pesticides. The best results were obtained in the acid pH range (3), and with contact time of 360 minutes.

For the contact time of 360 minutes (time of equilibrium) and pH 3, atrazine had an adsorption percentage of 82.35% for *Q. cerris* cork and 74.64% for *Q. suber* cork. Chlorpyrifos showed 84.05% of adsorption for *Q. cerris* cork and 80.54% for *Q. suber* cork. For lambda-cyhalothrin, the percentage of adsorption was 85.05% for *Q. cerris* cork and 81.76% for *Q. suber* cork. Fluazifop-P-butyl reached 84.25% adsorption with *Q. cerris* cork and 80.79% with *Q. suber* cork. Finally, lactofen reached 88.65% removal in solutions with *Q. cerris* cork and 76.82% for solutions with *Q. suber* cork. In general, the two corks showed similar adsorption
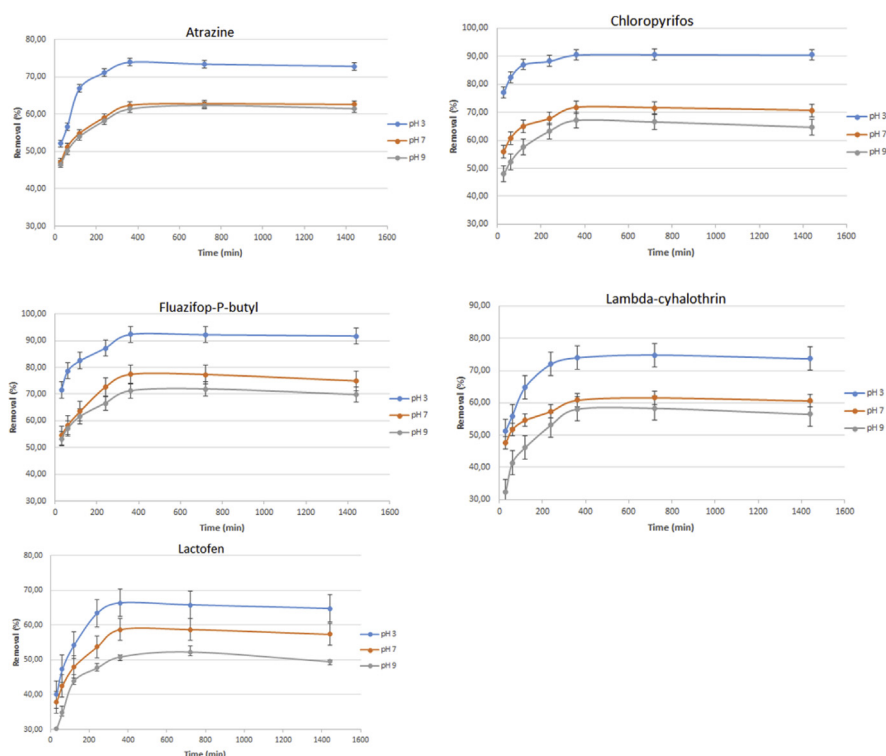

Fig. 3. Variation of pesticide removal efficiencies by *Q. suber* cork at different pH values.

characteristics, but certain pesticides such as atrazine and chloropyrifos showed some selectivity between these adsorbents (Fig. 4).

It is well known that adsorption processes are affected by pH and contact time (Moreno-Castilla, 2004). The pH determines the degree of distribution of the chemical species in solution. The intensity of this effect may be higher or lower depending on the adsorbent type. Surface charge of the adsorbent which depends on solution pH and the surface characteristics of the adsorbent plays an important role in adsorption (Moreno-Castilla, 2004). The surface charge of the cork at pH values lower than 4.4 was found to be positive implying protonated surface (Şen et al., 2012). Liu et al. (2015) observed higher atrazine adsorption on biochars at alkaline solution than at acidic pH conditions. The lower atrazine removal at acidic conditions was explained by the strong affinity between protonated biochar surface and atrazine.

Previous studies showed that the biosorption rate of pesticides on cork decreases with time after the main sites for adsorption become occupied. The adsorption mechanism was decribed in three-steps: bulk diffusion (I), internal diffusion (II) and adsorption (III). The biosorption of organic pollutants on biomass generally shows a pseudo-first order kinetic model and the equilibrium is achieved at long contact times between 20 and 48 h (Domingues et al., 2007; Villaescusa et al., 2011; Pintor et al., 2012).
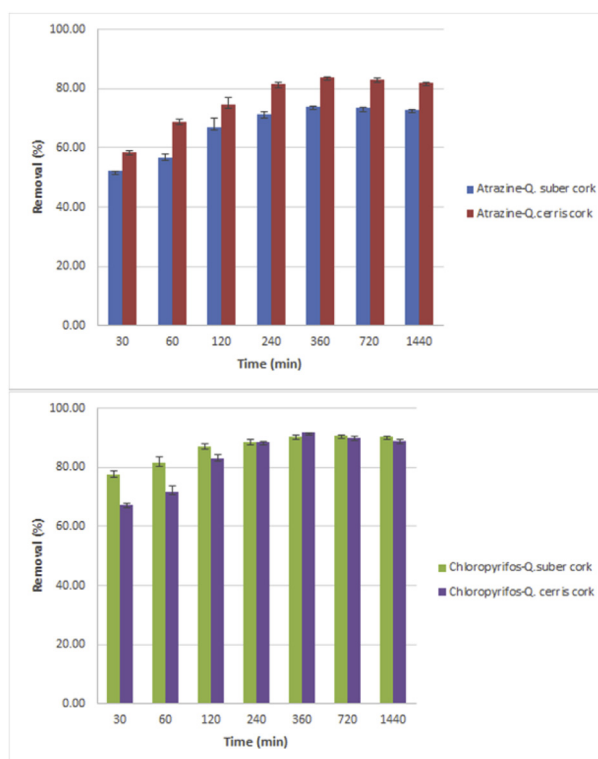

Fig. 4. Comparison of atrazine (above) and chloropyrifos (below) removal efficiencies by *Q. suber* and *Q. cerris* corks at different pH values.

3.2. Effect of temperature

In aqueous adsorption systems, the temperature is a determining factor, mainly affecting the rate of adsorption. An increase in the temperature increases the kinetic energy and the mobility of the adsorbate species, and causes an increase in diffusion rate of the adsorbate (Şen et al., 2012). The results of the analysis of the influence of temperature on the adsorption of pesticides through the corks of *Q. cerris* and *Q. suber.* are shown in Figs. 5 and 6. There was no significant difference between the different temperatures tested on adsorption efficiency ($p > 0.05$). However, the results demonstrated a subtle increase in efficiency at temperatures of 30 °C.

The temperature tests were performed at the best contact time and pH (360 minutes and pH 3). When the temperature was raised in the solution, the adsorption efficiency was also increased, reaching an ideal temperature of 30 °C for all the tests. After this temperature, the removal efficiencies began to fall, possibly due to the increased chemical potential of the pesticides, and by reduced density of the water, favoring a high desorption of the pesticides.

At 30 °C, the atrazine removal efficiencies were 83% for corks of *Q. cerris* and 73% for *Q. suber*. The chlorpyrifos already obtained 91% of adsorption for the cork of *Q. cerris* and 90% for the cork of *Q. suber*. For lambda-cyhalothrin the percentage of adsorption was 77% for *Q. cerris* cork and 74% for *Q suber* cork. Fluazifop-P-butyl
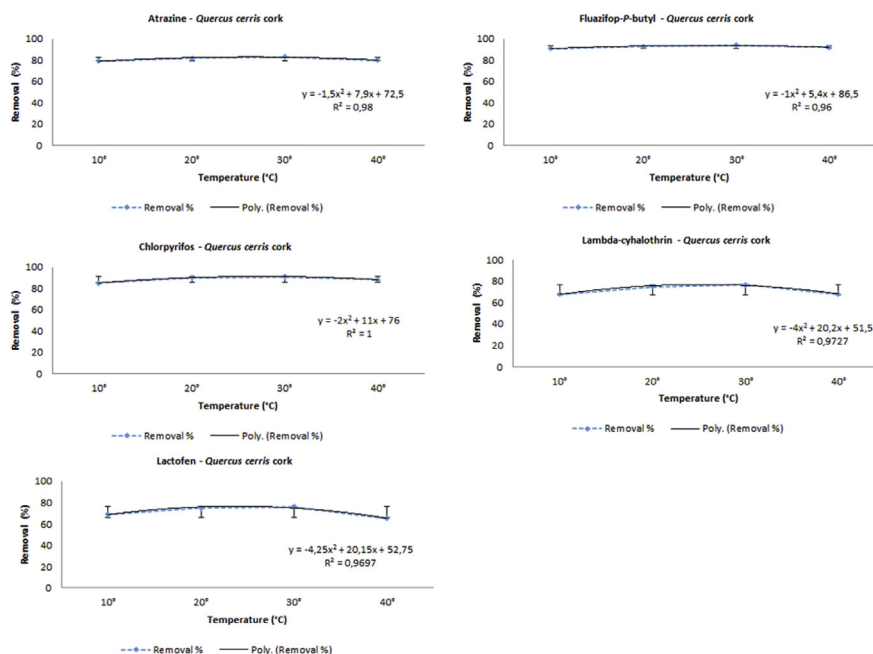

Fig. 5. Effect of temperature on pesticide removal efficiencies of *Q. cerris* cork at different temperatures.
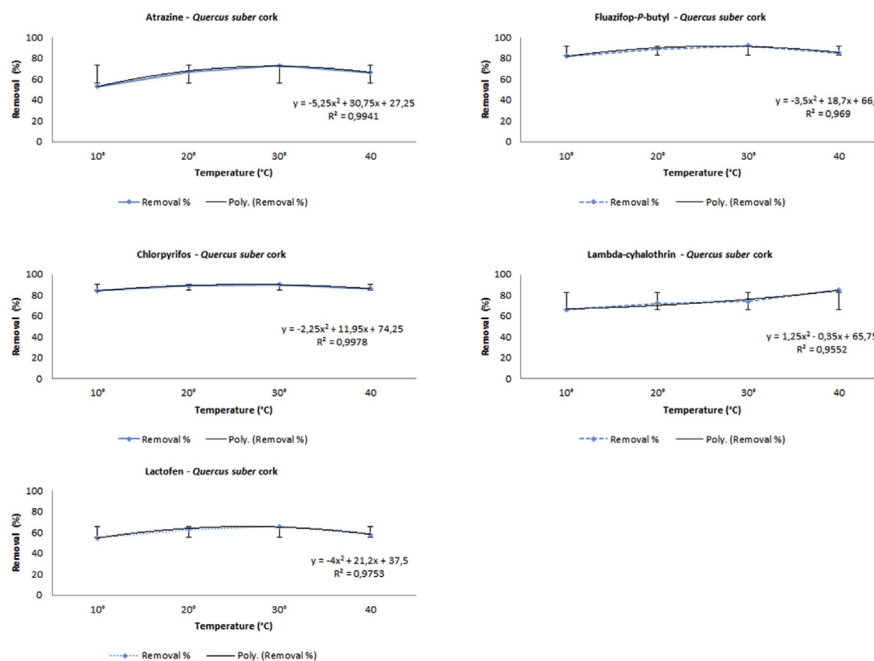
Fig. 6. Effect of temperature on pesticide removal efficiencies of *Q. suber* cork at different temperatures.

with the use of *Q. cerris* cork reached 94% and 92% removal with the use of *Q. suber* cork. Finally, lactofen reached 76% removal in solutions with *Q. cerris* cork and 66% for solutions with *Q. suber* cork. The increase in the efficiency of the removal is explained by Khattri and Singh (1999) who consider that the increase in temperature can affect the solubility and chemical potential of the adsorbate. In this way, increasing temperature leads to a change in adsorption capacity. Promoting an increase in temperature increases the mass diffusion rate of the adsorbate molecules in the pores of the adsorbent particles, due to the decrease in the viscosity of the solution. In addition, the temperature variation may initiate a pore opening process within the adsorbent structure, allowing the penetration of larger molecules of the adsorbate, thus increasing the adsorbent removal efficiency (Doğan et al., 2006).

3.3. Adsorption kinetic models

The pseudo-first-order kinetic models generally fit well with the sorption data. The reaction rate constant values varied from 0.55 to 1.42 while correlation coefficients were in the order of 0.90 (Table 3). These results are in agreement with the previous studies of adsorption of pesticides by different adsorbents (Ho, 2006; Villaescusa et al., 2011). Another interesting result was the adsorption kinetics of atrazine which fitted better with pseudo-second-order kinetics (Table 4). This difference may be due to the higher mobility of atrazine in relation to the other pesticides studied.

Table 3. Rate constants and regression coefficients for pseudo-first-order model.

Pesticides	*Q. suber* cork	
	k1	R^2
Atrazine	0.72	0.923
Chlorpyrifos	0.87	0.898
Fluazifop-P-butyl	1.42	0.983
Lactofen	1.20	0.886
Lambda-cyhalothrin	0.55	0.865

Table 4. Rate constants and regression coefficients for pseudo-second-order model for atrazine adsorption.

Adsorbents	k2	R^2
Q. suber cork	0.55	0.995
Q. cerris cork	0.23	0.988

4. Conclusions

The *Q. cerris* and *Q. suber* corks can be used as biosorbents for atrazine, chlorpyrifos, lambda-cyhalothrin, fluazifop-P-butyl, and lactofen in aqueous environments showing average removal efficiencies between 80% and 70%, for the studied pesticides, respectively. The influence of pH on the pesticide removal efficiencies was significant. The corks of *Q. cerris* and *Q. suber* have the highest pesticide sorption efficiencies at acidic conditions of pH 3 and at a temperature of 30 °C. The pesticides were adsorbed on cork following pseudo-first-order and pseudo-second-order kinetics.

The overall results show that the corks of both species can be used for the treatment of pesticide contaminated waters as an alternative method to the expensive pesticide removal techniques that are currently being used.

Declarations

Author contribution statement

Terencio R. de Aguiar Junior: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

José Osmar A. Guimarães Neto, Ali Umut Şen: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Helena Pereira: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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