SORPTION PERFORMANCE OF *QUERCUS CERRIS* CORK WITH POLYCYCLIC AROMATIC HYDROCARBONS AND TOXICITY TESTING

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Quercus cerris is an important oak species extended in large areas of Eastern Europe and Minor Asia that has a thick bark which is not utilized at all. The sorption performance of cork from *Quercus cerris* bark with four polycyclic aromatic hydrocarbons (PAHs) (acenaphthene, fluorene, phenanthrene, and anthracene) was investigated. *Quercus cerris* cork was characterized for elemental analysis, acidic groups, and summative chemical composition, and the results were compared with *Quercus suber* cork. A Microtox® test was carried out to test for the release of any toxic compounds into the solution. All isotherms fit the Freundlich model and displayed linear *n* values. *Quercus cerris* exhibited a high efficiency for sorption of PAHs for the studied concentrations (5 to 50 µg/L) with 80-96% removal, while the desorption isotherms showed a very low release of the adsorbed PAHs (<2%). In relation to *Quercus suber* cork, K_F values of *Quercus cerris* cork are about three times lower. The quantity of *Quercus cerris* cork required to reduce water pollution by PAHs was estimated to be less than twice the quantity of other adsorbents such as aspen wood and leonardite. Toxicity tests indicated that non-toxic compounds were released into the solution by the *Q*uercus *cerris* and *Q*uercus *suber* cork samples. Overall the results indicate the potential use of *Quercus cerris* cork and of *Quercus suber* cork as effective and economical biosorbents for the treatment of PAH-contaminated waters.

Keywords: Quercus cerris; Quercus suber; Biosorbent; Sorption-desorption; Polycyclic aromatic hydrocarbons (PAHs); Toxicity

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are contaminants that originate from the combustion of fossil fuels. Highly suspected to be probable carcinogens, they are transported by the atmosphere into surface waters (Olivella 2006). Because of their persistence and low solubility they may be accumulated in the food chain (García-Falcón and Simal-Gándara 2005; García-Falcón et al. 2005; Rey-Salgueiro et al. 2007; Rey-Salgueiro et al. 2009a,b). Although activated carbon is probably one of the most effective conventional methods for the removal of PAHs from water (Derbyshire et al. 2001;

Kyriakopoulos y Doulia 2006), the treatment of large amounts of wastewater and stormwater streams makes the treatment highly expensive.

In recent years there has been an increasing interest in removing contaminants, including PAHs, from aqueous environments with low-cost materials. The use of low-cost sorbents and the search of available natural materials are very attractive in terms of their contribution to decrease the costs of operation, therefore helping environmental protection. Depending on the hydrophilic or hydrophobic character of the contaminant, different materials have been applied (Rodríguez-Cruz et al. 2009). The most common adsorbent used so far has been activated carbon, but other cost-efficient and effective options have been tested (Olivella et al. 2011; Ratola et al. 2003; Boving and Zhang 2004; Domingues et al. 2005; Wang et al. 2006; Zeledón et al. 2007).

One of the cost-effective organic materials that has been used to remove PAHs from wastewaters is cork, an industrial raw material extracted from the bark of cork oak trees (*Quercus suber*) and known worldwide as the material used to seal wine bottles (Pereira 2007). Cork is mainly composed of lignin and suberin (hydrophobic biopolymers) and hydrophilic polysaccharides (cellulose and hemicellulose). This heterogeneous chemical composition provides numerous bonding possibilities for a wide range of pollutants.

The cork industry is highly dependent on one application and, therefore dependent on the fate of the stopper market which has lost a big share to alternative closures, aluminum screw caps, and synthetic stoppers. In fact, wine corks only represent 15% of the cork usage by weight but 66% of the revenue. The significant amounts of low-cost residues generated by the cork industry are valued for insulation and surfacing purposes, but their capacity to remove liquid contaminant has also been demonstrated (Domingues et al. 2005; Olivella et al. 2011; Psareva et al. 2005). While cork oak is the species currently providing cork, the bark of other oak species, such as the Turkey oak (*Quercus cerris*), also contains substantial, albeit not continuous, regions of cork and may therefore be considered as a new source of cork (Şen et al. 2010, 2011a). Cork from *Quercus cerris* has cellular and chemical features similar to those of cork from *Quercus suber* and can be used as an adsorbent even though the differences require a different experimental approach.

In this study, the sorption performance regarding PAHs from water environment of *Quercus cerris* cork has been investigated and compared to cork from *Quercus suber* and to other sorbent materials. In addition, acidic surface functional groups were characterized, and tests were carried out to assess the toxicity of aqueous solutions after contact with both *Quercus cerris* and *Quercus suber* cork samples in the same conditions used in the PAH sorption experiments in order to study a potential release of toxic substances from the sorbents into the solution.

EXPERIMENTAL PROCEDURE

Samples

The *Quercus cerris* cork samples were obtained from the bark of trees that were 70 to 80 years old, in the Andırın district of Kahramanmaraş province, in the southeastern

part of Turkey. The cork layers within the *Quercus cerris* bark were separated manually from the phloem regions within the periderms (Şen et al. 2011b).

The *Quercus suber* cork sample was taken from factory-supplied cork strips originating from boards of reproduction cork used to produce stoppers. The cork strips were cut into three layers with a hand saw at three radial positions: the outermost layer (the back), 6-10 mm thick; the middle part used for cork stoppers, 26-32 mm thick; and the innermost layer of cork (the belly), 3-5 mm thick. In this study, only the belly layer was used (Jové et al. 2011).

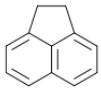
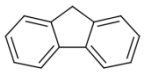
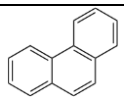
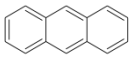
Each sample was cut into small pieces (<10 mm) and milled using a ZM-200 ultracentrifugal mill (Retsch). The granulated samples were sieved, and the 40-60 mesh granulometric fraction (0.25-0.42 mm grain size) was used for the subsequent analyses.

Reagents

Standard samples of selected PAHs (acenaphthene, fluorene phenanthrene, and anthracene) and deuterated phenanthrene (phenanthrene-d_{10}) at concentrations of 500 μg/mL each one and 2000 μg/mL, respectively were purchased from Supelco (Bellefonte, PA, USA). Chemical properties of the selected PAHs are shown in Table 1.

Deionized water was used for standard solutions and batch experiments. Methanol was Super Purity grade from Romil (Cambridge, UK). Solid phase microextraction (SPME) fibers of 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) were supplied by Supelco (Bellefonte, PA, USA).

Table 1. Chemical Properties of Selected PAHs for this Study. Values presented are obtained from Mackay et al. (2004).

	Name	Abbreviation	Structure	M_w g/mol	logK_{ow} [a]	S [b] mg/L
1	Acenaphthene	Ace		154.21	3.92	3.8
2	Fluorene	Flu		166.2	4.18	1.9
3	Phenanthrene	Phe		178.24	4.57	1.1
4	Anthracene	Ant		178.24	4.54	0.045

[a] K_{ow} is the octanol-water partition coefficient
[b] S is the solubility

Characterization of the Cork Samples

The C, H, N, and S contents were determined using a Perkin Elmer EA2400 series II elemental analyzer. Oxygen content was calculated by mass difference. The H/C, O/C, C/N, and (O + N)/C atomic ratios were calculated. The detection limits for N and S were 1.20% and 0.44%, respectively.

Acidic surface properties of the cork were determined by the Boehm method (Psareva et al. 2005). According to Boehm, the acidic surface properties derive from the presence of different surface groups: both strong and weak carboxyl groups, carbonyl, lactonic, enolic, and phenolic groups. These groups have different acidity: strongly acidic (carboxylic groups), versus weakly acidic (carboxylic, lactonic and enolic). Acidic groups can be differentiated by neutralization with solutions of $NaHCO_3$, Na_2CO_3, and NaOH. According to the protocol only strongly acidic carboxylic acid groups are neutralized by sodium bicarbonate; those neutralized by sodium carbonate are lactones, lactol, and the carboxylic groups (strong and weak acidic groups). The weakly acidic phenolic groups only react with strong alkali, such as sodium hydroxide. Thus, the difference between NaOH and Na_2CO_3 consumption corresponds to the weakly acidic phenolic group, and the difference between the values for Na_2CO_3 and for $NaHCO_3$ corresponds to the concentration of the weak carboxylic groups.

The chemical characterization of the samples included determinations of: extractives using dichloromethane for solubilization of aliphatic extractives and ethanol and water for extraction of phenolics; suberin; total lignin, including acid insoluble and soluble lignin; and holocellulose. The methods for the chemical characterization of these samples have been described elsewhere (Şen et al. 2010; Jové et al. 2011).

Adsorption Isotherms

For sorption studies in this research, four PAHs were analyzed: acenaphthene [Ace], fluorene [Flu], phenanthrene [Phe], and anthracene [Ant]. The batch equilibrium technique was used for the adsorption experiments. A sample of 0.3 g of cork was weighed into a Pyrex glass bottle and put into contact with 100 mL of an aqueous solution of a PAH mix with different concentrations (5, 10, 20, and 50 μg/L). In all the cases the methanol concentration in solution was 1% or lower. Four points were enough in the studied range for the calculation of isotherms due to the acceptable linearity and reproducibility obtained (< 10%). In a previous study, the equilibrium time for *Quercus suber* was one hour (Jové et al. 2011) and in this study for *Quercus cerris* less than two hours (data not shown). To ensure the full sorption process three hours was chosen as equilibrium time.

The glass bottles were closed, wrapped with aluminum foil, and mixed with a "Vibromatic" shaker at 700 oscillations/min. After shaking, liquid aliquots of 18 mL were collected using a glass luer tip syringe of 20 mL coupled to a stainless steel syringe needle (length 6 in., size 22 gauge) and analyzed for the PAH content, as described below. The amount of adsorbed PAH was considered to be the difference between the initial PAH concentration of the solution and the PAH concentration in the liquid phase at equilibrium.

Three blanks were performed following the same procedure used for the samples: (1) 100 mL of deionized water plus 1 µg/L PAHs; (2) 0.3 g of cork plus 100 mL of deionized water; and (3) 100 mL of deionized water.

Sorption data were fitted to the Freundlich equation in the linearized form according to the equation $\log q = \log K_F + n \log C_{eq}$, where q is the adsorbed amount (µg/g); C_{eq} is the equilibrium concentration of adsorbate in solution after adsorption (µg/L); K_F is an indication of the adsorbent capacity $[(\mu g/g)/\mu g/L)]^{1/n}$; and n is the nonlinearity coefficient.

The distribution coefficient (K_d) is the ratio between the content of the substance in the solid phase and the mass concentration of the substance in the aqueous solution when adsorption equilibrium is reached. K_d values were calculated from the slope of the isotherms.

Desorption Isotherms

Desorption isotherms were studied to assess the degree of reversibility of the sorption process. In the adsorption experiments after equilibrium was attained, the aqueous phase was removed by vacuum filtration and the contaminated cork was put in a glass bottle with 100 mL of deionized water. The content of this bottle was shaken during 6 h, and the solution was analyzed, following the same procedure used for the sorption isotherms.

Solid Phase Microextraction (SPME) and GC-MS Analysis

The extraction of PAHs and the GC-MS analysis were performed following the procedure described by Fernández et al. (2007). For the SPME extraction, 18 mL of deionized water in 20 mL vials, capped with polytetrafluoroethylene (PTFE)-coated septa were analyzed. The fibers were immersed into the aqueous phase with agitation at 60°C for 60 min. After extraction, the fiber was thermally desorbed for 10 min into the liner of the GC injector port at 300°C. The splitless time was set at 4 min, and the desorption time at 10 min. GC was performed with a 6890N Agilent chromatograph equipped with a MPS2 Gerstel autosampler and coupled to a MS 5973N mass spectrometer. The separation was achieved using an HP-5MS column (30m, 0.25mm, 0.25µm film thickness) (J&W Scientific, Folsom, CA, USA), and the GC oven program was: 50°C (3 min), increased by 6°C/min to 325°C (held for 20 min). The carrier gas was helium (99.999%) from Abello Linde with a constant flow rate of 1 mL/min. The transfer line temperature was set at 300°C and the ion source temperature at 250°C. The mass spectrometer was operated in selected ion monitoring mode (SIM). The quantification of PAHs was based on comparisons of the areas for the monitored molecular ions to that of the internal standard, with calibration response curves generated from five different concentrations (0.05, 0.1, 0.5, 1, and 5 µg/L) of each target PAH. The calibration curves for the compounds were linear ($r > 0.99$) over the established range.

Ecotoxicity Test

The possible toxicity added to the solution due to the eventual release of components from the cork was tested with the standard Microtox® bioassay. This test, which consists of measuring the decrease in light emission by *Vibrio fischeri* bacteria

exposed to noxious chemicals, is claimed to be reliable, rapid, and sensitive. Although the toxicity is not commonly controlled in low-cost sorbents, it should be essential to check it, especially in wastes that have suffered some kind of processes. Indeed, extractives of cork with hot water have been reported to show an acute toxicity ranging from 4.1 to 12.3 toxic units for bacterium *Vibrio fischeri* (Anselmo et al. 2001). Some phenolic extractives, namely the group of tannins, are responsible of this toxicity (Mendonça et al. 2004).

After 0.3 g of cork was mixed with 100 mL of deionized water and exposed to 1 h adsorption contact time, an aliquot of 10 mL was collected from each glass bottle, filtered, and analyzed using ecotoxicity tests. Both *Quercus suber* and *Quercus cerris* cork samples were tested. The pH of the samples were between 6 and 8, as required for the Microtox experiments.

The tests were performed using the Microtox Model 500 Toxicity Analyzer System from Azur Environmental (Carlsbad, USA) following the protocols for the basic or 100% test, according to the standard operating procedure (Azur Environmental 1998). The freeze-dried luminescent bacteria, reconstitution solution, osmotic adjusting solution (OAS), diluent, and cuvettes were purchased from Azur Environmental (Carlsbad, USA). Light measurements were taken at 0, 5, and 15 minutes.

The toxicity analyzer is equipped with a 30-well temperature-controlled incubator block set at 15°C and a storage cell kept at around 5°C for the reconstituted bacteria before dilution. The light intensity was digitally recorded. The test consists of adding 10 µL of reagent (Vibrio fischeri bacteria) to four different dilutions of the sample after their osmotic adjustment to get 2% NaCl concentration, which is the required medium for the bioassay. The sample concentration in the four tested dilutions is within the range 45 - 6.25%. A blank consisting in ultrapure water adjusted at 2% NaCl is used to assess the loss of light due to time of exposure. Light measurements were taken at 5 and 15 minutes. The effective concentration, EC50, at which a 50% loss of light emission is observed, is determined with a 95% level of confidence by using the Gamma (Γ) function, which is defined as the ratio of light lost to light remaining, by a specific computer program. The EC50 is the concentration at which Γ=1 (Microbics corporation 1992).

The freeze-dried luminescent bacteria, reconstitution solution, osmotic adjusting solution (OAS), diluent, and cuvettes were purchased from Azur Environmental, (Carlsbad, USA).

RESULTS AND DISCUSSION

Characterization of the Cork Samples

Given that lignin, containing primarily aromatic moieties, and extractives showed great affinity for PAHs (Wang et al 2007; Olivella et al. submitted), a *Quercus suber* sample with a similar percentage of lignin and total extractives was selected for comparison in the sorption studies (Jové et al. 2011). The elemental composition and chemical composition of the *Quercus cerris* and *Quercus suber* cork samples are shown in Table 2.

Table 2. Chemical Composition, Elemental Analysis and Atomic Ratios of Cork from *Quercus suber* and *Quercus cerris*

	Quercus suber	*Quercus cerris*
Extractives*		
Aliphatic, %	5.6	10.9
Phenolic, %	10.8	5.8
Suberin, %	44.1	28.5
Total lignin, %	25.7	28.1
Holocellulose, %	5.0	16.5
Elemental analysis		
C, %	61.0	50.7
H, %	8.7	7.3
Atomic ratios		
H/C	1.70	1.73
O/C**	0.37	0.62

*Aliphatic extractives were extracted with dichloromethane and phenolic extractives were extracted with ethanol and water (Jové et al. 2011; Şen et al. 2010).
** Oxygen was calculated by the mass difference.

Carbon content was lower in the *Quercus cerris* cork sample (50.7 vs. 61.0%), leading to a much higher O/C ratio (0.62 vs. 0.37). The results for N and S were below the determination limits of the equipment and were therefore not considered.

The polarity coefficient (O+N)/C is an important parameter to predict sorption. This parameter was shown to be negatively correlated with the sorption capacity of biopolymers for hydrophobic pollutants (Wang et al. 2007). The values found here for the cork samples are in range of some commercial lignins (0.33-0.94) (Wang et al. 2007) and lower than those obtained for untreated aspen wood (0.754) (Huang et al. 2006).

The difference in elemental composition of the two corks derives from the differences in their chemical composition. Suberin content is higher in *Quercus suber* cork (44.1% vs. 28.5%), while the polysaccharide content is lower (5.0% vs. 16.5% measured as holocellulose). Since lignin content was rather similar in both cork samples, these differences explain the higher polarity of *Quercus cerris* cork.

The results obtained from the determination of acidic groups are listed in Table 3.

Table 3. Distribution of Acidic Functional Groups in Cork from *Quercus suber* and *Quercus cerris*

	Surface Acid Concentration, mmol/g	
	Quercus suber	*Quercus cerris*
Total acid groups	1.8805	1.5520
Strong acids	0.7330	0.8520
Phenolic OH groups	0.9155	0.6815
Weak acid groups	0.2320	0.0185

It is shown that *Quercus suber* cork has a higher concentration of total acidic groups (1.88 mmol/g and 1.55 mmol/g). This difference is mainly attributed to the concentration of phenolic groups and weak carboxylic groups. The content of strong acid groups was, however, higher in *Quercus cerris* cork, in accordance with its higher content of hemicellulosic polysaccharides.

In comparison with other natural materials the total acidic groups found in these *Quercus* samples were in the range of those found in the husk of the mango pit (1.38 mmol/g) and lower than those found in a mango pit/seed (3.15 mmol/g) (Elizalde-González and Hernández-Montoya 2007).

Adsorption/Desorption Isotherms

Adsorption isotherms of PAHs for the *Quercus cerris* cork were obtained (Fig. 1). The equilibrium sorption curves for PAHs fit the Freundlich equation well, following an almost linear C-type curve according to the classification of Giles et al. (1960). The C-type isotherms point to a partitioning mechanism of the adsorbate in the adsorbent, and have been seen for different pesticides (Iglesias et al. 1997; Rodríguez-Cruz et al. 2007), phenols (Ahmaruzzaman and Sharma 2005), and chlorophenols (Severtson and Banerjee 1996).

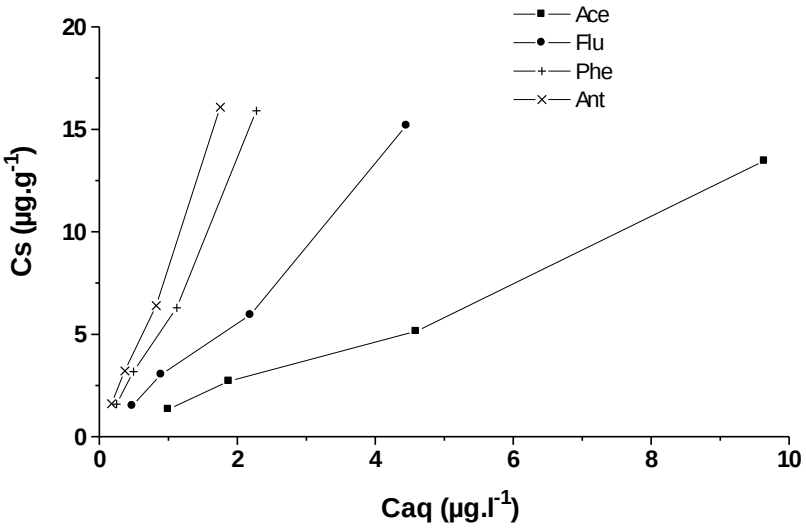


Fig. 1. Adsorption isotherms of acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), and anthracene (Ant) of cork from *Quercus cerris*

A high percentage of removal was obtained (Table 4), indicating a large affinity of the cork to remove PAHs, and a high effectiveness of the adsorption treatment of the contaminated aqueous solutions.

The sorption coefficients (K_F) for the four tested PAHs, Ace<Flu<Phe<Ant, increased by a factor of about six between Ace and Ant. This trend is in relation to the different polarities of the PAHs. For the *Quercus suber* cork sample the sorption coefficients were K_F = 5 for Ace, K_F = 11 for Flu, K_F =21 for Phe, and K_F =23 for Ant. Thus, *Quercus suber* cork exhibits higher affinity (about three times more) for sorption of

these PAHs than *Quercus cerris* cork. The lower holocellulose content in *Quercus suber* cork (5%) than in *Quercus cerris* cork (16.5%) would favor adsorption because it is located in the primary cell wall and the formation of water clusters via H-bonding could prevent the access of molecules to the bonding sites.

Table 4. Adsorption Coefficients of PAHs on *Quercus cerris* Cork Determined by the Freundlich Equation (K_F, n), correlation coefficients (r), distribution coefficients (K_d), and mean removal percentage calculated at 1, 5, 10, 20, and 50 µg/L

PAHs*	K_F±SD ([(µg/g)/µg/L)]$^{1/n}$)	n±SD**	r	K_d (L/g)	% Removal
Ace	1.4±0.2	1.03±0.02	0.98	1.3±0.1	80
Flu	3.2±0.4	1.01±0.02	0.99	3.3±0.2	90
Phe	6.4±1.0	0.98±0.03	0.99	6.8±0.6	95
Ant	8.8±1.0	1.02±0.02	0.99	8.9±0.9	96

*Abbreviations: acenaphthene [Ace], fluorene [Flu], phenanthrene [Phe], anthracene [Ant]
** SD, standard deviations of triplicate experiments.

The desorption isotherms (not shown) were also well fitted to the Freundlich equation. Table 5 shows the desorption coefficients.

Table 5. Desorption Coefficients of PAHs on *Quercus cerris* Cork Determined by Freundlich Equation (K_{FD}, n_D), Coefficients of Determination (r^2) and Mean Percentage of PAHs Released into the Solution Calculated at 5, 10, 20, and 50 µg/L

PAHs*	K_{FD}±SD ([(µg/g)/µg/L)]$^{1/n}$)	n_D±SD**	r^2	% Released
Ace	33±4	1.02±0.01	0.98	0.99
Flu	23±1	0.96±0.02	1.00	1.53
Phe	77±4	1.02±0.05	1.00	0.41
Ant	97±5	1.08±0.05	1.00	0.27

* Abbreviations: acenaphthene [Ace], fluorene [Flu], phenanthrene [Phe], anthracene [Ant]
** SD, standard deviations of triplicate experiments.

The K_{FD} values (sorbed amounts of PAHs remaining after desorption) were greater for Phe and Ant, which are less soluble (1.1 mg/L and 0.045 mg/L, respectively) than Ace and Flu (3.8 mg/L and 1.9 mg/L, respectively). After a predetermined equilibrium desorption time of 6h, both samples released low percentages of PAHs into the solution (<2%), reflecting the difficulty of PAH desorption from the cork matrix.

Estimation of Sorbent Usage

Table 6 shows the amount of *Quercus cerris* and *Quercus suber* cork that is required to reduce PAHs pollution of 1 L of water from 50 μg/L to 0.1 μg/L. The amount of *Quercus cerris* cork needed is about 1.4 times less than the amount of leonardite and 2 times less than the amount of aspen wood fibers; it is however 3 to 4 times higher than the amount of *Quercus suber* cork. Thus, the results indicate that *Quercus cerris* could be used as an effective biosorbent for the removal of PAHs from wastewater. In addition, its utilization would give an added-value to this natural material.

Table 6. Comparison of the Amount of Biosorbent Needed to Reduce PAHs Pollution from 50 μg/L to 0.1 μg/L and Comparison with Other Materials Reported in the Literature

PAHs*	*Quercus cerris* usage (g/L)	*Quercus suber* (g/L)	Aspen wood fibers usage (g/L)	Leonardite usage (g/L)
Ace	334	80		
Flu	153	39		218 [b]
Phe	82	22	166 [a]	
Ant	54	20		

* Abbreviations: acenaphthene [Ace], fluorene [Flu], phenanthrene [Phe], anthracene [Ant]

a) Huang *et al.* 2006

b) Zeledón *et al.* 2007

Ecotoxicity test

Emission of light by the bacteria after 5 and 15 minutes of contact with 45% (the upper concentration that can be tested in the Microtox® basic test protocol) of both *Quercus suber* and *Quercus cerris* cork suspensions decreased by 25%. The same light emission decrease was observed in the control solution (ultrapure water). Therefore, EC_{50} could not be calculated by the computer program, and both *Quercus suber* and *Quercus cerris* cork suspensions were considered as being non-toxic to the bacteria. These results put into evidence that the use of both corks as sorbents does not contribute to any additional toxicity to the treated PAH-contaminated water.

CONCLUSIONS

The sorption performance of *Quercus cerris* cork in relation to polycyclic aromatic hydrocarbons (PAHs) in aqueous solutions was assessed and compared to that of *Quercus suber* cork. Results obtained indicate that:

1. *Quercus cerris* exhibits a high percentage of removal for the selected PAHs (80-96%).
2. The total acidic groups was quantified as 1.552 mmol/g.
3. The amount of *Quercus cerris* used to reduce a PAH-water contaminated was less than twice the amount of leonardite and aspen wood and between 3 and 4 times higher the *Quercus suber* sample.
4. No significant toxicity could be detected by using the bioassay Microtox® test when the concentration of both types of cork in the sample was 3 g/L.

The results obtained in this study are the basis for future studies based on the use of the *Quercus cerris*, whose bark is not used at all, as an effective and economical biosorbent for the removal of PAHs in PAH-contaminated waters. Future studies are mainly focused on developing a technology based on cork filters for treatment of stormwater.

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