

# Valorisation of Cork By-Products for the Treatment of Vegetal and Animal Oil containing Wastewaters

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## Abstract

In this study, cork granules, which are by-products of the cork processing industry, were used as biosorbents for the removal of vegetable and animal oils from water. Simple oil-in-water emulsions were created by ultrasonic emulsification and batch adsorption tests were performed by contacting cork with these emulsions for a defined period of time. A mass transfer model was able to predict adequately the kinetic data, using a Linear Driving Force approximation for intraparticle diffusion and equilibrium described by the Langmuir-Freundlich equation. Maximum sorption capacities for vegetable and animal oil, as calculated by the Langmuir-Freundlich model, were  $5 \pm 4$  and  $2.3 \pm 0.9$  g g<sup>-1</sup>, respectively. Therefore, expanded cork granules proved to be an efficient, low-cost sorbent for both vegetable and animal oils.

**Keywords:** sorption; cork by-products; oily wastewaters; water reuse.

## Introduction

The treatment and discharge of wastewaters containing oil and grease is an emerging environmental problem, because these waters cannot be submitted to traditional treatment, as they may create problems at wastewater treatment plants, such as creation of grease interfaces in the equipment and interferences in the biological process (Ahmad et al. 2005b). Unfortunately, this problem gets worse every year due to rising urbanization and industrial development (Srinivasan and Viraraghavan 2010).

There are a lot of different industrial sources of wastewaters contaminated with oil and grease, such as oil refineries, the metal-working industry and the food processing industry. In the latter, the grease in the wastewaters is from animal or vegetal origin, and results from several activities, such as slaughtering, cleaning and transforming operations (Patterson 1985). Oil and grease in these wastewaters is often in the range of thousands of mg L<sup>-1</sup> (Yang 2007).

In general, oil and grease can be divided into four types (Patterson 1985): free oil, mechanical dispersions, chemically stabilized emulsions and “dissolved oil” (i.e., dispersed in very fine drops). Free oil can be easily separated by gravity methods, which are often referred to as primary treatment. However, this is not the case with emulsions, for which the finer the oil drops, the more difficult they are to destabilize. The breaking of the oil-water emulsion can be done by chemical methods (coagulation (Ahmad et al. 2006), acidification, dissolved air flotation (DAF) (Patterson 1985)), electrical methods (electroflotation, electrocoagulation (Yang 2007)), and physical methods

(centrifugation (Srinivasan and Viraraghavan 2010), filtration (ultrafiltration, reverse osmosis) (Al-Jeshi and Neville 2008; Rhee et al. 1989)). More recently, the possibility of using adsorption for removal of oil has been gaining popularity, the adsorbents ranging from activated carbon (Dalmacija et al. 1996; Hami et al. 2007) to organoclays (Al-Malah et al. 2000; Alther 1995) and biosorbents (i.e., biomass or wastes, such as chitosan (Ahmad et al. 2005b), barley straw (Ibrahim et al. 2009; Ibrahim et al. 2010), walnut shells (Srinivasan and Viraraghavan 2008) and rubber powder (Ahmad et al. 2005a)).

Using dead biomass or waste products of agricultural or industrial activities as biosorbents has been a recently favored practice for removing pollutants from wastewater by sorption. In Portugal and other Mediterranean countries, the cork industry is a leading economic activity that generates several types of cork by-products, from crude cork impurities to cork granules in a wide range of particle sizes (Gil 1997). Cork consists in the outer bark of the cork oak tree, known botanically as *Quercus suber* L., and cork powder is produced throughout the different stages of industrial processing, especially grinding, cutting and sanding operations (Silva et al. 2005).

Although it is a porous material, cork has scarce or null pore interconnectivity, and it shows some unique properties such as high coefficient of friction, resilience, imperviousness to liquids, low thermal conductivity, low density, high energy absorption, excellent insulation properties, near-zero Poisson coefficient, and resistance to fire, among others (Fernandes et al. 2010; Pereira 1988). These are caused by its microscopic and chemical composition features, which differ from other lignocellulosic materials. The structure of cork is formed by hollow polyhedral prismatic cells, which have a honeycomb shape when observed from the radial direction (relative to the tree trunk) and rectangular when viewed from transversal directions. The chemical composition of cork consists primarily of suberin and lignin, the other organic constituents being polysaccharides (cellulose and hemicellulose) and extractives (waxes and tannins) (Pintor et al. 2012). It is believed that the high percentage of suberin on cork (33-62%) is responsible for its hydrophobicity, which has been observed in studies of surface polarity (Silva et al. 2005), adsorption of water vapor (Lequin et al. 2010) and sorption of organic pollutants (Domingues et al. 2007; Karbowski et al. 2010).

Due to the interesting physical and chemical characteristics of cork aforementioned, and since cork granules are at the present time being successfully used commercially as a sorbent for oil spills (CORTICEIRA AMORIM 2009), it can also have good potential for sorbing oil and grease in wastewaters. Therefore, this work aims to study the kinetics and equilibrium uptake of commercial vegetal and animal oils into cork granules.

## **Material and Methods**

### *Biosorbents*

The expanded cork granules were provided by CORTICEIRA AMORIM, SGPS (Portugal) in a granulometry range between 2 and 4 mm. The material was washed twice in 2-hour cycles at 60°C using distilled water, in order to remove impurities and other water extractable components that may interfere with the sorption process. Before usage, the biomass was dried at 60°C during a 24-hour period.

### *Oil-in-water emulsions*

The oil-in-water emulsions at the desired concentration ranges were prepared by ultrasonic emulsification of weighted amounts of commercial vegetable oil (*Froiz-Sol* refined sunflower oil) or commercial animal oil (*Seven Seas* cod-liver oil) and 150 mL of distilled water, using a Hielscher UP400S Ultrasonic Processor, with cycle time 0.75 and amplitude of 75% within periods of 1 minute for each emulsion.

### Batch biosorption equilibrium isotherms

In order to compare the sorption capacity of the biomass for both types of oil, equilibrium experiments were carried out by contacting 150 mL of oil-in-water emulsions with 0.25 g L<sup>-1</sup> of expanded cork granules in 250 mL Erlenmeyer flasks, during 15 hours (optimized equilibrium time), at room temperature (25.0 ± 0.1°C) under constant magnetically stirring. The initial concentrations of oil were selected to enable the derivation of sorption isotherms, and varied between 100 mg L<sup>-1</sup> and 2000 mg L<sup>-1</sup>. The experiments were performed in duplicate, and oil and grease concentration in the remaining emulsions was quantified using the partition-infrared method described in methods 5520-C and 5520-F from Standard Methods Manual (2005).

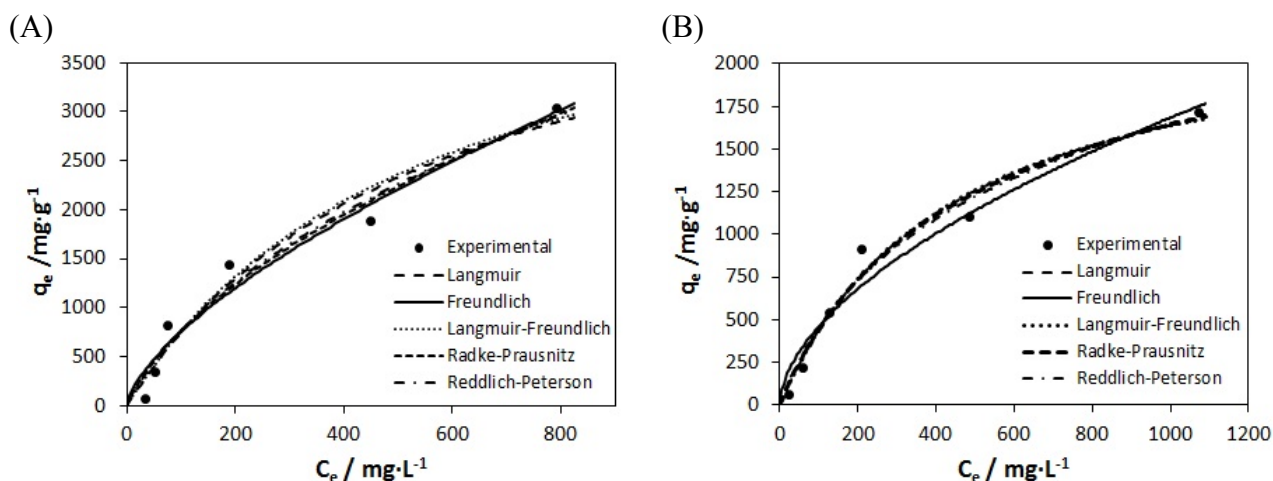
### Batch biosorption kinetics

The kinetics of oil removal by cork were studied in duplicate for both types of oil. For each experiment, 150 mL of oil-in-water emulsions containing 600 mg L<sup>-1</sup> of oil were taken in 250 mL Erlenmeyer flasks and 0.25 g L<sup>-1</sup> of expanded cork granules were added. Samples were withdrawn at appropriate times over the course of 24 hours, and the oil and grease concentrations were determined by partition-infrared methods 5520-C and 5520-F from the Standard Methods Manual (2005) for quantification of the oil removed at different intervals.

## Results and Discussion

### Equilibrium studies

The amount of oil on expanded cork granules as a function of its concentration at equilibrium conditions is shown in Figure 1, for both commercial vegetable oil (Figure 1A) and animal oil (Figure 1B).



**Figure 1.** Biosorption equilibrium isotherms for (A) vegetable oil and (B) animal oil on expanded cork granules. Conditions: particle size = 2-4 mm, contact time = 15 h, temperature = 25.0±0.1°C, pH = 7.0±0.2

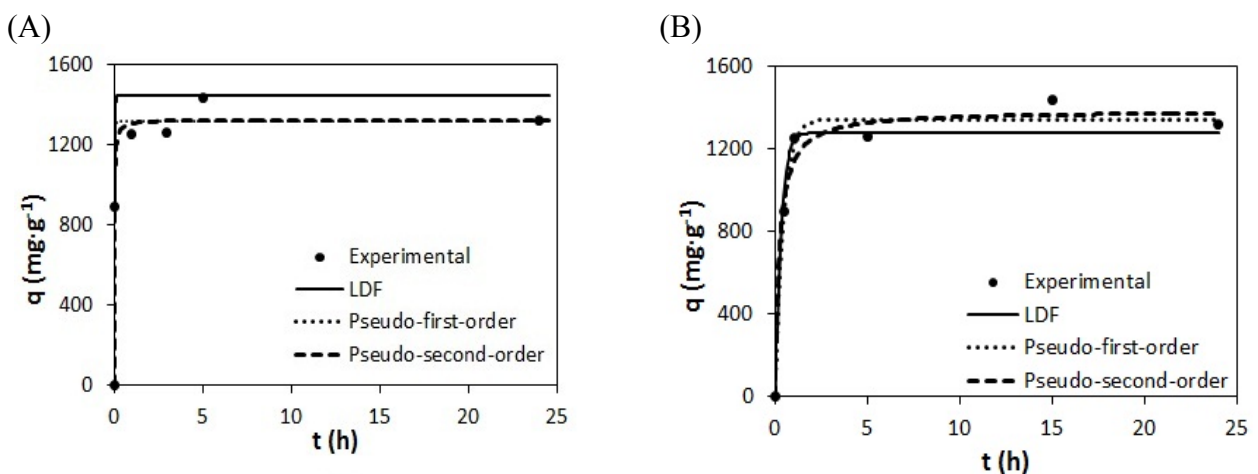
For the better understanding of the adsorption mechanism, as well as to assess the adsorption characteristics and magnitude, it is necessary to find a suitable fitting model. Several isotherm models, namely Langmuir (1918), Freundlich (1907), Langmuir-Freundlich (Sips 1950), Radke-Prausnitz (1972) and Redlich-Peterson (1959), were fitted to the equilibrium data, as can be seen in Figure 1. These models attempt to explain the phenomena occurring within the solid-liquid interface, and they relate the equilibrium concentrations experimentally observed on both solid and liquid phases. For detailed information about these models please refer to the corresponding literature. The suitability of the models was compared by statistical F-test with a 95% confidence level, and revealed that the difference between the models was not significant. In general, it is seen that the Langmuir-Freundlich isotherm could reasonably fit the data for both case studies, and therefore the results are discussed on the basis of the Langmuir-Freundlich model. However, as the Langmuir-Freundlich dimensionless parameter indicative of the intensity of the adsorption corresponds to  $n_{LF} = 1$ , the isotherm model used becomes equivalent to the Langmuir model. The corresponding parameters are shown in Table 1.

**Table 1.** Summary of the Langmuir-Freundlich parameters for oil sorption on cork

Langmuir-Freundlich Model				
	$q_{LF}$ ( $\text{g}\cdot\text{g}^{-1}$ )	$k_{LF}$ ( $\text{L}^{1/n}\cdot\text{mg}^{-1/n}$ )	$n$	$r^2$
Vegetable Oil	$5 \pm 4$	$(2 \pm 2) \times 10^{-3}$	$1.0 \pm 0.5$	0.955
Animal Oil	$2.3 \pm 0.9$	$(2 \pm 2) \times 10^{-3}$	$1.0 \pm 0.3$	0.975

### Kinetic studies

The prediction of the rate-limiting step is an important factor when designing an adsorption process. For a solid-liquid sorption process, the solute transfer can be either characterized by external mass transfer (boundary layer diffusion) for nonporous medium, intraparticle diffusion for porous medium, or both mechanisms (Acheampong et al. 2011). Kinetic studies help to identify the adsorption process and to predict, as well as to control, the efficiency of the wastewater treatment mechanism. Commonly, they are based on the pseudo-first-order and pseudo-second-order models by Lagergren (1898), which are still widely applied nowadays. Both pseudo-first-order and pseudo-second-order rate equations are based on the sorption capacity of the solid-phase, and more information about these models can be found in detail in the literature (Ho 1995; Lagergren 1898).



**Figure 2.** Evolution of sorbed vegetable oil (a) and animal oil (b) on expanded cork granules. Conditions: particle size = 2-4 mm, temperature =  $25.0 \pm 0.1^\circ\text{C}$ , pH =  $7.0 \pm 0.2$ , initial concentration =  $600 \text{ mg}\cdot\text{L}^{-1}$

Both models were fitted to the experimental kinetic data, as can be seen in Figure 2. The kinetic parameters related to the models can be determined from the non-linear fitting of the experimental data, and thus the kinetic parameters obtained from the models for each type of oil, as well as the correlation coefficients, are shown on Table 2. The applicability of both kinetic models was compared by using the statistical F-test with a 95% confidence level, and showed no statistical difference between them. However, when comparing the experimental and predicted equilibrium uptake capacities, the pseudo-first-order model seems to fit the data better, with higher correlation coefficient for the animal oil.

A mass transfer model was developed considering the first and widely used approximation for spherical sorbent particles originally proposed by Gleuckauf and Coates (1947), the Linear-Driving-Force model (LDF). Considering that the sorption rate in the spherical particle is controlled by the LDF model, the mass transfer model imposes external film diffusion as negligible and oil equilibrium between solid and liquid phases, as formulated by the Langmuir-Freundlich equation. The ordinary differential equations used to compute analytically the mass transfer coefficient in the generalized LDF approximation can be seen in detail in Vilar (2006). The LDF fitting to the experimental data is presented in Figure 2, and the computed mass transfer coefficient values are shown in Table 2.

**Table 2.** Summary of the kinetic model parameters for oil sorption on cork

<b>Kinetic Models</b>			
<b>Lagergren pseudo-first-order</b>			
	$q_e$ (mg·g <sup>-1</sup> )	$k_{1,ads}$ (h <sup>-1</sup> )	$r^2$
Vegetable Oil	$(1.32 \pm 0.04) \times 10^3$	$38 \pm 6$	0.985
Animal Oil	$(1.34 \pm 0.04) \times 10^3$	$2.3 \pm 0.3$	0.987
<b>Lagergren pseudo-second-order</b>			
	$q_e$ (mg·g <sup>-1</sup> )	$k_{2,ads}$ (g·mg <sup>-1</sup> ·h <sup>-1</sup> )	$r^2$
Vegetable Oil	$(1.32 \pm 0.04) \times 10^3$	$0.05 \pm 0.01$	0.986
Animal Oil	$(1.38 \pm 0.06) \times 10^3$	$0.003 \pm 0.001$	0.979
<b>Linear-Driving-Force</b>			
	$k_p \times a_p$ (h <sup>-1</sup> )	$\tau_d$ (h)	
Vegetable Oil	$17 \pm 6$	$0.9 \pm 0.3$	
Animal Oil	$1.4 \pm 0.3$	$10 \pm 2$	

As shown in Figure 2, the LDF model fits satisfactorily the kinetic data for both types of oil; however the fitting to the animal oil data considered the error associated with the adsorption capacity determined by the Langmuir-Freundlich isotherm. The intraparticle homogeneous diffusion coefficient  $D_h$  was calculated assuming the average particle size as 3 mm. For vegetable oil,  $D_h = (7 \pm 2) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , while for animal oil  $D_h = (6 \pm 1) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ .

## Conclusion

In this study, expanded cork granules proved to be a good sorbent for both vegetable and animal oil. Biosorption equilibrium of both types of oil to cork by-product is achieved in less than 5 hours of contact time. The Linear Driving Force model was used to describe the kinetic data and a good fitting was achieved. Adsorption isotherms fitted reasonably well to several models, including the Langmuir-Freundlich one. Maximum sorption capacities for vegetable oil and animal oil on cork as calculated by the Langmuir-Freundlich model were  $5 \pm 4$  and  $2.3 \pm 0.9 \text{ g g}^{-1}$ , respectively.

In short, it can be concluded from this study that sorption of vegetable and animal oil on cork is a viable process to remove oil from oil-in-water emulsions, with the advantage of being a by-product. Further studies are needed to probe the applicability of this process on real oily wastewater problems, namely multi-pollutant systems, and demonstrate its technical and economic feasibility.

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