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TREATMENT OF WASTEWATER CONTAINING MINERAL OIL BY SORPTION ONTO GRANULATED CORK

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The aim of this work is the development of a new method to remove oils from wastewaters, namely hydrocarbons. These contaminants, when present in high concentrations, are efficiently removed by physical and chemical processes, such as gravity separators, flocculation and flotation processes; however for low concentrations, these methods are not applicable [1]. Moreover, advanced separation processes such as membrane separation [2] and activated carbon adsorption [3] are expensive options for the treatment of oil-containing wastewaters. This new technique is based on oil and hydrocarbons' sorption on cork granules. Such material is a by-product of the cork industry and it is available in a wide range of granulometries with different densities [4].

This research aims at optimizing the sorption process to remove oil from wastewater by establishing the best conditions for operation. A simulated wastewater was created for this study by ultrasonic emulsification of mineral oil in water at the desired concentration range. Preliminary tests were carried out to study the influence of the following variables: type of cork (natural or expanded); particle size; solid-liquid ratio; temperature, pH and ionic strength. Sorption kinetics and equilibrium isotherms were obtained using the optimum conditions. Tests were performed in batch mode at constant temperature of 25 °C, by contacting 150 mL of synthetic emulsion with 0.04 g of cork granules (2-4 mm) for a 24 hour period in order to establish equilibrium. Quantification of oil and grease remaining in solution was performed by partition-infrared method according to methods 5520-C and 5520-F in *Standard Methods* [5].

The equilibrium experiments were performed in duplicate for a range of mineral oil concentrations between 100 mg L^{-1} and 2000 mg L^{-1}. Freundlich, Langmuir-Freundlich, Radke-Prausnitz and Redlich-Peterson models were fitted to the equilibrium data for oil sorption on expanded cork, as shown in Figure 1.

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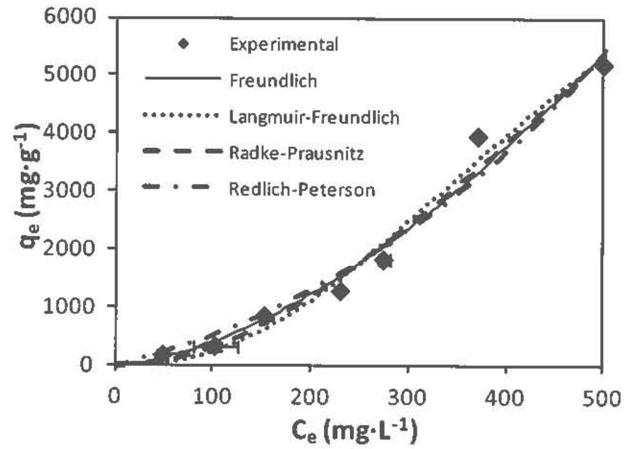

Figure 1. Experimental and predicted isotherm for the sorption of emulsified mineral oil in water using expanded cork.

The adequacy of the four models was compared by using the statistical *F*-test, for 95 % confidence level. Results show that the difference is not significant. Therefore, results are discussed on the basis of Langmuir-Freundlich parameters: $q_{LF} = (1.0 \pm 0.7) \times 10^4$ mg g^{-1}; $K_{LF} = (0.4 \pm 0.4) \times 10^{-6}$ L$^{1/n}$ mg$^{-1/n}$; $n_{LF} = (4 \pm 1) \times 10^{-1}$.

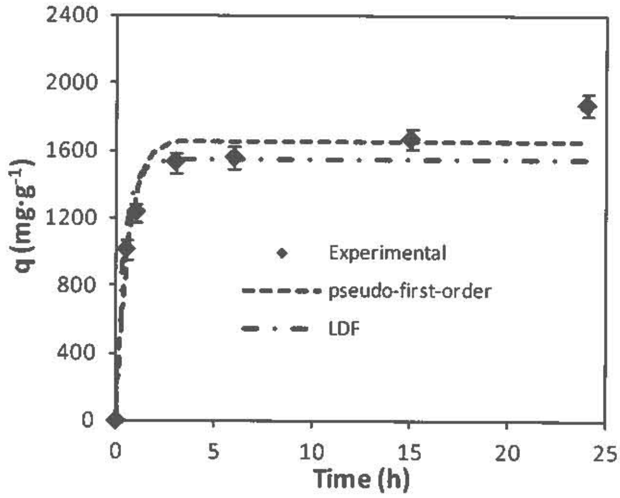

Figure 2. Experimental and predicted kinetic curves for the sorption of emulsified mineral oil in water using expanded cork ($C_{i,oil}$ = 600 mg L^{-1}).

Removal of mineral oil is faster at the initial 5-hours stage (Figure 2). The pseudo-first-order and pseudo-second-order models were fitted to the experimental kinetic data. The applicability of both models was compared by using the *F*-test, thus, showing that differences are not statistically significant. However, when comparing the experimental and predicted equilibrium uptake capacities, the pseudo-first-order model seems to be better. A mass transfer model was developed considering sorption rate in the spherical particle controlled by a Linear-Driving-Force model (LDF), negligible external film diffusion and equilibrium between bounded and soluble oil concentrations, as formulated by the Langmuir-Freundlich equation. The intraparticle homogeneous diffusion coefficient ($D_h = (1.5 \pm 1.3) \times 10^{-7}$ $cm^2\ s^{-1}$) and diffusion time ($\tau_d = 43 \pm 37$ h) were calculated assuming the particle diameter as 3 mm.

In this study, expanded cork proved to be a good sorbent for mineral oil, with high capacity (exceeding 5 $g\ g^{-1}$) and fast uptake.

Acknowledgements

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