

CORK BYPRODUCTS AS SORBENTS OF MINERAL OIL IN OIL-IN-WATER EMULSIONS

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ABSTRACT – This study evaluates the use of cork granulates as sorbents of oil and grease (O&G) in mineral oil-in-water emulsions. Regranulated cork granules showed faster kinetics and higher sorption capacities than raw cork granules for mineral oil; this can be associated to the increase of carbon content due to the thermal treatment (350-400°C), leading to the extraction of phenolic compounds and increment of the surface hydrophobicity. Sorption kinetic studies indicated that oil sorption onto the surface of regnanulated cork is favoured in acidic conditions. A partition/linear model was able to describe well the equilibrium data, achieving organic-carbon-normalized partition coefficients between (pH = 6.0) $3.3 < \log K_{OC} < 4.1$ (pH = 2.0). The maximum regnanulated cork experimental sorption capacity at pH 4.0 was 270 mg g⁻¹ considering an initial oil concentration of 110 mg L⁻¹. A mass transfer model, considering equilibrium given by a linear model, film diffusion resistance and instantaneous surface equilibrium was able to predict adequately the kinetic data.

1. INTRODUCTION

Mineral oil is a hazardous substance when discharged in water nevertheless its consumption in the world is around 42 million tons per year (APETRO, 2014). Bartz (1998) reported that about 13% of the total lubricant volume returns to the environment. Lubricant oils are a type of mineral oils used in automotive, mechanical and metalworking industries which typically contain hydrocarbons and aromatics base oils and less than 10% additives which improve tribology performance.

Oil and grease in wastewaters can exist in three forms: free, dispersed or emulsified, differing, basically, on oil droplet size. In an oil-water mixture, free oil is characterized by droplet sizes greater than 150 µm, dispersed oil has a size range of 20-150 µm and emulsified oil has droplets typically less than 20 µm. Free oil can be easily separated by gravity methods, which are often referred to as primary treatment. However, this is not the case with dispersed or emulsified oil, for which the finer the oil droplets, the more difficult they are to destabilize. The breaking of oil-water emulsions can be done by chemical methods, electrical methods, and physical methods. Adsorption processes have been gaining popularity in the treatment of oil-water emulsions, through the use of activated carbon, organoclays and different kinds of low cost materials called biosorbents (i.e., biomass or wastes, such as chitosan (Ahmad et al., 2005), barley straw (Ibrahim et al., 2010) and walnut shells (Srinivasan and Viraraghavan, 2008)).

Cork and cork by-products, besides being sustainable and renewable materials, also show unique properties such as hydrophobicity, resilience, and resistance to fire, among others (Fernandes et al., 2010), and have been utilized as sorbent for heavy metals, pesticides, radionuclides, phenolic compounds and SO₂ (Pintor et al., 2012). Apart from raw cork, cork-based activated carbons prepared by chemical or/and thermal methods have been shown to have good sorption capacities (Pintor et al., 2012). Portugal, which holds about 60% of the total cork oak forest area, provides about 80% of the cork produced in the World (Gil, 2009).

This research aims to study the removal of mineral oil from oil-water emulsions using raw and regranulated cork granules as sorbent materials, in order to comply with discharge limits into receiving water bodies established by Portuguese (15 mg/L, (Decreto-Lei nº 236/98)) and Brazilian agencies (20 mg/L, (CONAMA, 2005)). Kinetic and equilibrium studies at batch system were performed at different pH values. A mass transfer model, considering equilibrium given by a linear model, film diffusion resistance and instantaneous surface equilibrium was applied to describe the kinetic data in a batch system.

2. EXPERIMENTAL

2.1. Materials

Two types of cork granules were used in this study: raw cork (0.8 -1.0 mm) and regranulated cork (1.0 – 2.0 mm), both supplied by Corticeira Amorim SGPS. The production of regranulated cork granules includes a thermal treatment of raw cork at 380° C with injection of water vapor.

The raw cork granules were 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, both type of granules were dried at 60°C during a 24-hour period.

2.2. Oil-in-water emulsions

Oil-in-water emulsions were prepared by shearing diluted mixtures of commercial motor oil (15W40 gas/Diesel, brand: CONTINENTE) in distilled water at 8800 rpm using a rotor-stator mixing device (UltraTurrax MICCRA D-15, ART), in three 10-minute cycles separated by 10-minute breaks. The pH of oil-in-water emulsions was adjusted to the predefined values (2.0, 4.0 or 6.0) right after shearing, through acidification with H₂SO₄ (0.05, 0.5 or 5 M). No further pH adjustment was done throughout the experiment and the final values were measured. O&G concentration was measured using the partition-infrared method (5520-C of Standard Methods) by Fourier Transform Infrared Spectrometry (FTIR) (IRAffinity-1, Shimadzu) with spectra acquired in the range 2700-3200 cm⁻¹ and using tetrachloroethylene as the extraction solvent.

2.3. Sorption Studies

Sorption kinetic experiments were carried out in 50-mL conic capped glass tubes containing 45 mL of emulsion (~110 mg MO L⁻¹) in contact with 45 mg of cork granules

(liquid/solid ratio of 1 g L⁻¹). The tubes were placed in a rotating shaker at 20 rpm, inside a thermostatic cabinet at a constant temperature of 25 °C. Samples were collected at predetermined time intervals, up to a contact time of 24 hours, and residual MO concentration was determined by FTIR.

The amount of mineral oil sorbed at each time per unit mass of sorbent (q_t , mg MO g⁻¹ sorbent) was determined using the mass conservation balance to the batch system (Eq. 1):

$$q_t = \frac{V}{W} (C_0 - C_t) \quad (1)$$

where V (L) is the volume of emulsion, W (g) is the dry weight of the sorbent, C_0 (mg L⁻¹) is the initial MO concentration in the emulsion and C_t (mg L⁻¹) is the MO concentration in the emulsion at time t .

Sorption isotherms at 25 °C were obtained by changing the solid/liquid ratio from 0.2 g L⁻¹ to 2.2 g L⁻¹ using an initial MO concentration of ~110 mg MO L⁻¹. Runs were carried out in triplicate during 16 hours (necessary time to reach the equilibrium) and the average values were taken into account.

3. RESULTS AND DISCUSSION

3.1. Sorption kinetics

Preliminary sorption kinetic tests were performed using raw and regranulated cork materials. Fig. 1 shows that MO sorption kinetics are faster using regranulated cork than using raw cork, achieving also higher MO uptake capacities. Such behaviour is mainly associated to the higher hydrophobicity and carbon content of regranulated cork due to the thermal treatment (350-400°C) which enhances the extraction of phenolic compounds. Sorption kinetic studies also indicated that oil sorption onto the surface of regranulated cork is favoured in acidic conditions.

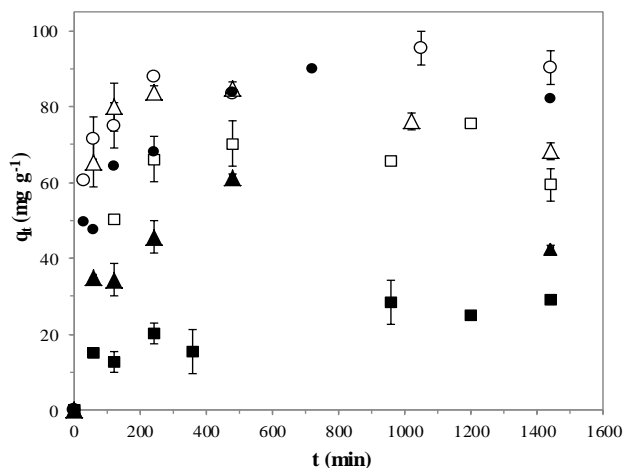


Figure 1 – MO sorption kinetics using raw (■- pH 6.0, ▲- pH 4.0, ● - pH 2.0) and regranulated cork samples at different initial pH values (□- pH 6.0, △- pH 4.0, ○ - pH 2.0).

3.2. Sorption isotherms with regranulated cork

Fig. 2 shows the sorption isotherms at different pH values using the regranulated cork material. Freundlich model, represented by Eq. (2), was able to fit well the equilibrium data.

$$q_e = K_F C_e^{1/n} \quad (2)$$

where C_e and q_e are the equilibrium concentrations of MO in liquid (mg L^{-1}) and solid phase (mg g^{-1}), K_F ($\text{mg}^{(1-1/n)} \text{L}^{1/n} \text{g}^{-1}$) is an indicator of the adsorption capacity and n is an empirical parameter of the Freundlich equation that indicates sorbate-sorbent affinity.

At Table 1, Freundlich constant n decreases with pH decrease, indicating that sorbate-sorbent affinity is higher at pH 2. The linear equilibrium model is also able to describe well the experimental data (Fig. 2), and it enables the calculation of partitioning coefficients K , which measures the partitioning of an organic compound (mineral oil) between solid (cork material) and water.

Literature reports that the sorption of hydrophobic organic compounds can be correlated to the organic content of the solids, suggesting that the process is an organic-organic partitioning (Karickhoff et al., 1979). The organic-carbon-normalized partition coefficient, K_{oc} , can be calculated by dividing the partition coefficient (K) by the fraction of organic carbon in the regranulated cork (Table 2). Pintor et al., (2013) showed that regranulated cork presents an organic carbon fraction of 70%.

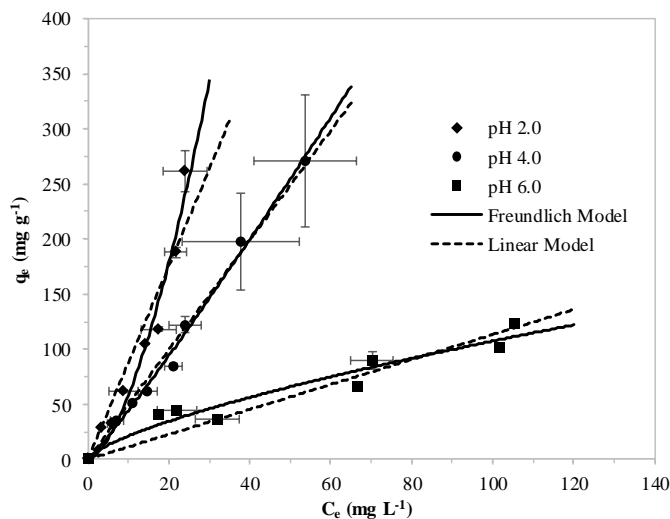


Figure 2 - Equilibrium sorption experimental data points and equilibrium model lines.

Table 1 – Freundlich and Linear equilibrium model parameters.

pH	Model Parameters						
	Freundlich Model				Linear Model		
	K_F ($\text{mg}^{(1-1/n)} \text{L}^{1/n} \text{g}^{-1}$)	n	R^2	S_R^2 (mg g^{-1}) ²	K (L g^{-1})	R^2	S_R^2 (mg g^{-1}) ²
2.0	1 ± 1	0.7 ± 0.1	0.96	352	8.8 ± 0.7	0.91	717
4.0	3.4 ± 0.7	0.92 ± 0.05	0.99	72	5.0 ± 0.1	0.99	91
6.0	4 ± 2	1.4 ± 0.3	0.92	122	1.13 ± 0.07	0.89	178

Karickhoff et al., (1979) showed a relationship between K_{oc} and octanol-water partition coefficient (K_{ow}) for a series of polycyclic aromatics and chlorinated hydrocarbons, represented by Eq. (3):

$$K_{oc} (\text{L kg}^{-1}) = 0.63 \times K_{ow} \quad (3)$$

Table 2 shows that when decreasing the solution pH from 6.0 to 2.0 the organic-carbon-normalized partition coefficient increases more than six times, which could indicate a neutralization of oil droplets repulsive forces, consequently higher oil coalescence and more affinity to these new oil droplets to cork surface under acid conditions.

Normally, octanol-water partition coefficients for hydrocarbons vary between 1 and 7 (Grathwohl, 1990; Isnard and Lambert, 1989); and according to Ahel and Giger (1993), alkylphenol (AP), one of the lubricant additives present in the mineral oil used in this work, has a $\log K_{ow} = 4.1$, which is similar to values found in this work (Table 2).

Table 2 – Mineral oil Partition coefficients for reggranulated cork.

pH	$K_{oc} (10^3 \text{ L kg}^{-1})$	$\log K_{ow}$
2.0	13.0 ± 0.7	3.9 ± 0.2
4.0	7.0 ± 0.1	3.7 ± 0.9
6.0	2.00 ± 0.07	3 ± 1

3.3. Sorption kinetics modelling

It is important to be able to predict the rate at which pollutants are removed from aqueous solutions in order to design a sorption treatment plant. Cork materials are characterized by low surface areas mainly associated to the external macropores with an honeycomb structure. As the interior cork cells are closed, cork has no available internal porosity. Preliminary studies using pure oil showed an instantaneous sorption on the surface of cork materials. Based on these properties, a mass transfer model was developed considering the following assumptions: oil equilibrium between solid and liquid phases is formulated by the partition law (Eq. 4), isothermal process, spherical cork particles, negligible intraparticle diffusion (instantaneous equilibrium) and

external fluid film resistance.

$$q^* = K \times C^* \quad (4)$$

where q^* is the MO concentration on the surface of the solid phase (mg g^{-1}), K is the partition coefficient (L g^{-1}) and C^* is the MO concentration in the liquid phase at the surface of the sorbent (mg L^{-1}).

Mass balance to the batch contactor:

$$-V \frac{dC_b}{dt} = W \frac{dq}{dt} \quad (5)$$

where C_b is the concentration of MO in bulk of the liquid phase (mg L^{-1}), V is the reactor volume (L), W is the mass of sorbent (g), t is time (s) and q is the concentration of MO on the solid phase (mg g^{-1}). Considering local equilibrium, $q = q^*$.

Due to the characteristics of oil-in-water emulsions, in which small oil droplets are dispersed in water, cork can act as a filter promoting coalescence of small oil droplets around the cork particles, favouring the oil trapping by capillary forces in the sorbent macropores. Considering the formation of an external sublayer around the cork particles, in which the solute diffuses from the bulk fluid to the surface of the particles, the following equation can be established:

$$\frac{dC_b}{dt} = -\frac{1}{\tau_f} \times (C_b - C); \tau_f = \frac{\varepsilon_b}{1 - \varepsilon_b} \frac{1}{k_f \times a_p}; a_p = \frac{3}{r_p} \quad (6)$$

where k_f is the film mass transfer coefficient (cm s^{-1}), a_p is the external surface area per unit particle volume ($\text{m}^2 \text{m}^{-3}$), ε_b is the bulk porosity, r_p is the particle radius (m) and τ_f is the time constant for film diffusion (s).

Replacing Eqs. 4 and 5 in 6 and solving for q , the following expression can be obtained:

$$q = \frac{q_0}{(1 + \zeta_m)} \left\{ 1 - \exp \left[- \left(\frac{1 + \zeta_m}{\zeta_m} \right) \cdot \frac{t}{\tau_f} \right] \right\}; \zeta_m = \frac{W \times q_0}{V \times C_{b_0}}; q_0 = K \times C_{b_0} \quad (4)$$

where ζ_m is the mass batch capacity factor and q_0 is the MO concentration at the solid phase in equilibrium with the initial MO concentration in the liquid phase (C_{b_0}) (mg g^{-1}).

Removal of MO is faster at the initial stage and gradually decreases until it reaches equilibrium in less than 200 minutes. The mass transfer model, considering equilibrium given by a linear model, film diffusion resistance and instantaneous surface equilibrium was able to predict adequately the kinetic data. The time constant for film diffusion increases with pH which indicates that low pH

values favours the coalescence of oil drops enhancing the sorption capacity and diffusion time (Table 3).

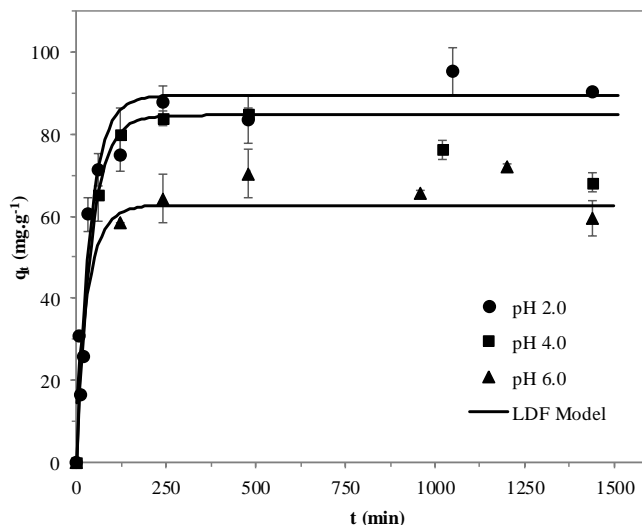


Figure 3 – Experimental kinetic data and simulated concentration profiles for MO uptake onto the cork surface.

Table 3 – Mass transfer model parameters

pH	Parameters	
	τ (min)	$k_f (10^3 \text{ cm s}^{-1})$
2.0	41	10
4.0	50	9
6.0	68	7

4. CONCLUSION

In this study, cork by-products proved to be good sorbents for oil and grease in mineral oil-in-water emulsions. Kinetic results showed that the thermal treatment of regranulated cork was able to improve MO sorption capacities and kinetic rates. A partition/linear model was able to describe well the equilibrium data, achieving organic-carbon-normalized partition coefficients between (pH = 6.0) $3.3 < \log K_{OC} < 4.1$ (pH = 2.0). A mass transfer model, considering equilibrium given by a linear model, film diffusion resistance and instantaneous surface equilibrium was able to predict adequately the kinetic data. The time constant for film diffusion increases with pH which indicates that low pH values favours the coalescence of oil drops enhancing the sorption capacity and diffusion time.

5. ACKNOWLEDGMENTS

This work was supported by project Pest-C/EQB/LA0020/2013 financed by FCT and FEDER through COMPETE, and by QREN, ON2 and FEDER. R. Souza acknowledges her

postdoctoral fellowship by CAPES (BEX-2615/13-4). A. Pintor acknowledges her PhD scholarship by FCT (SFRH/BD/70142/2010). V.J.P. Vilar acknowledges the FCT Investigator 2013 Programme (IF/01501/2013).

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