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Treatment of vegetable oil refinery wastewater by sorption of oil and grease onto regranulated cork – A study in batch and continuous mode

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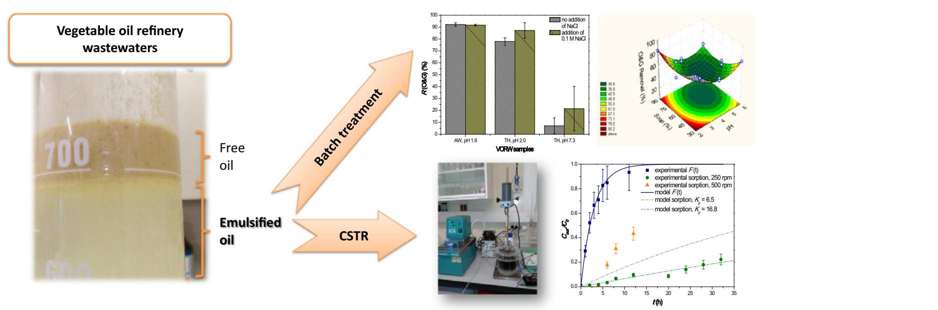
HIGHLIGHTS

- O&G removal from vegetable oil refinery wastewaters was successful at low pH.
- The presence of saponified matter inhibits O&G sorption onto regranulated cork.
- The occurrence of a filter effect enhanced O&G removal in a continuous stirred-tank.
- A mass transfer model describes O&G sorption kinetics in batch and continuous mode.

GRAPHICAL ABSTRACT



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ABSTRACT

The feasibility of a novel sorption treatment using regranulated cork granules for oil and grease (O&G) removal from real vegetable oil refinery wastewaters (VORW) was investigated and compared to similar treatment of oil-in-water emulsions.

O&G sorption from real VORW onto regranulated cork particles was studied at different pH and ionic strength conditions. Only wastewater acidification was able to effectively destabilize the O&G emulsion in the wastewater, enhancing the sorption process (efficiency over 80% at pH 2.0).

A 3-factor, 3-level (3^3) Box–Behnken experimental design was used to examine the effect of pH, ionic strength and soap/oil ratio on O&G removal efficiency in oil-in-water emulsions. All effects were significant ($p < 0.05$) when considered individually, but no significant interactions were observed. pH was found to have the strongest effect, supporting the initial observations in real VORW.

The treatment of a simulated wastewater (60% soap/oil ratio, 0.2 M NaCl and pH 2.0) was completed in batch and continuous mode. Freundlich and linear partitioning models were used to describe O&G sorption equilibria. Continuous treatment was successfully carried out in a stirred-tank reactor using a cork dosage of 3.4 g L^{-1}, a stirring speed of 250 rpm and a flowrate of 10 mL min^{-1}. The reactor was fed for 8 h with simulated wastewater (205 ± 30 mg L^{-1} O&G) yielding an effluent with an O&G content below 15 mg L^{-1} (discharge limit defined in Portuguese legislation). A mass transfer model was applied to describe the O&G sorption kinetics in batch and continuous stirred-tank reactors.

1. Introduction

Vegetable oils are a part of dietary requirements all over the globe, being widely used in food conservation and preparation.

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Nomenclature

List of acronyms

ANOVA	analysis of variance
AW	wastewater sample from the removal of waxes line
COD	chemical oxygen demand
CSTR	continuous stirred tank reactor
DAF	dissolved air flotation
DOC	dissolved organic carbon
FTIR	Fourier transform infrared spectroscopy
O&G	oil and grease
PVC	polyvinyl chloride
TH	wastewater sample from the homogenization tank
VORW	vegetable oil refinery wastewaters

List of symbols

adj-r^2	adjusted regression coefficient
a_p	external surface area per unit of particle volume (cm^2 - cm^{-3})
C_0	average feed O&G concentration ($mg\,L^{-1}$)
C_b	bulk O&G concentration in the reactor ($mg\,L^{-1}$)
C_{b_0}	initial O&G concentration in the bulk liquid ($mg\,L^{-1}$)
C_c	final O&G concentration in the control experiment ($mg\,L^{-1}$)
C_{eq}	O&G concentration at equilibrium ($mg\,L^{-1}$)
C_f	final O&G concentration in the sorption experiment ($mg\,L^{-1}$)
C_{in}	inlet O&G concentration ($mg\,L^{-1}$)
C_{out}	outlet O&G concentration ($mg\,L^{-1}$)
C_p	O&G concentration next to the sorbent surface ($mg\,L^{-1}$)
$F(t)$	normalized response/cumulative residence time distribution
k_f	film mass transfer coefficient ($cm\,s^{-1}$)
K_F	Freundlich constant ($mg^{(1-1/n)}\,L^{1/n}\,g^{-1}$)
K_p	partition coefficient ($L\,kg^{-1}$; $L\,g^{-1}$)
n	dimensionless parameter in the Freundlich equation related to sorbate–sorbent affinity
N_f	number of mass transfer units by film diffusion
P	pressure (atm)
q	sorption capacity; sorbed amount per unit mass ($mg\,g^{-1}$)
q_{eq}	sorption capacity at equilibrium ($mg\,g^{-1}$)
Q	flowrate ($L\,h^{-1}$)
r^2	regression coefficient
r_p	particle radius (cm)
R	O&G removal efficiency (%)
t	time of contact/operation (h; s)
T	temperature (°C)
V	volume in the batch or continuous reactor (L)
W	mass of sorbent (g)
x_1	independent variable, coded as NaCl concentration (M)
x_2	independent variable, coded as pH
x_3	independent variable, coded as soap ratio (%)
$\hat{y}$	predicted response of O&G removal efficiency (%)
y_b	dimensionless O&G bulk concentration
α	significance level
β_0	regression coefficient for the intercept
β_1	regression coefficient for the linear effect of x_1
β_{11}	regression coefficient for the quadratic effect of x_1
β_{12}	regression coefficient for the two-way linear interaction effect of x_1 and x_2
β_{13}	regression coefficient for the two-way linear interaction effect of x_1 and x_3
β_2	regression coefficient for the linear effect of x_2
β_{22}	regression coefficient for the quadratic effect of x_2
β_{23}	regression coefficient for the two-way linear interaction effect of x_2 and x_3
β_3	regression coefficient for the linear effect of x_3
β_{33}	regression coefficient for the quadratic effect of x_3
ε_b	bulk porosity
θ	dimensionless time
λ_1, λ_2	coefficients of the resolution of a second order homogeneous differential equation
ξ	mass capacity factor
ξ_m	batch mass capacity factor
ρ_{ap}	apparent density of the sorbent particles ($g\,L^{-1}$)
τ	mean residence time (h)
τ_{exp}	experimental mean residence time (h)
τ_f	time constant for film diffusion (s)
τ_{th}	theoretical mean residence time (h)

After extraction from plant seeds, the oils are refined before consumption in order to remove impurities and thus improve their taste and odour. Refining of vegetable oils, especially by chemical methods, generates large volumes of vegetable oil refinery wastewaters (VORW) which can be hazardous to the environment due to their high concentrations of oil and grease (O&G) [1].

Free oil in VORW has been shown to be successfully removed by a primary gravity separation treatment [2], but emulsified oil remains a challenge for a secondary treatment stage. Conventional treatment methods are ineffective, since oily matter is of difficult biodegradation [3]. Some authors have successfully completed biological treatment by providing an upstream physicochemical unit of coagulation/flocculation and sedimentation or dissolved air flotation (DAF) [1,4]; however, the production of hazardous sludge arising from the use of coagulant salts requires special handling and disposal [5]. Membrane technology has been proposed as an alternative treatment capable of high effluent purity and recovery of the oily retentate, but it is prone to fouling and needs expensive maintenance [5,6].

Removal of O&G by sorption is emerging as an alternative methodology for the treatment of oily wastewaters [7]. The use of activated carbon, which is favourable in many adsorption applications, is not successful for this purpose due to pore clogging effects [8], so other mineral adsorbents, such as organoclays, with smaller surface areas but higher surface hydrophobicity, have been used [7–9]. Recent studies report that natural organic sorbents, for instance chitosan [10], non-viable fungal cultures [11,12], dead plant biomass [13], and walnut shell [14], have equal or greater capacity than mineral sorbents and combine the environmental aspect of water decontamination with the reuse of byproducts or residues from agricultural and forest activities.

Cork, the outer bark of *Quercus suber* L., widely used for the fabrication of wine stoppers, is a material with favourable characteristics for oil uptake, due to its hydrophobicity [15]. Regranulated cork granules, byproducts of cork processing, have been shown to be good sorbents for O&G removal from oil-in-water emulsions as long as high ionic strength and/or low pH conditions are provided [16]. For practical application, a deeper study on whether these conclusions hold in a real wastewater matrix must be carried out.

The main difference between an oil-in-water emulsion and O&G in VORW is that the latter is more than just neutral vegetable oil; it is also composed of waxes, i.e. esters of longer chain fatty acids with high melting point, and soaps, sodium salts of fatty acids