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Modeling of supercritical CO₂ extraction of contaminants from post-consumer polypropylene: Solubilities and diffusion coefficients in swollen polymer at varying pressure and temperature conditions

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ABSTRACT

The reported work aimed at the modeling of the supercritical CO₂ (SCCO₂) extraction of contaminants covering a wide range of molecular weights from post-consumer polypropylene. A theoretical model taking into account the combined effects of the two essential phenomena involved in the extraction process (diffusion through the matrix and solubility in SCCO₂) is applied to experimental results in order to analyze extraction and disclose relevant kinetics limitations affecting extraction process. From fitting the model to the experimental data obtained at varying pressure and temperature conditions, information on diffusion coefficients of contaminants through polypropylene swollen by SCCO₂, activation energies for diffusion and solubilities in the supercritical fluid at temperatures of 50, 70 and 90 °C, and pressures of 100, 200 and 300 bar were obtained. Good agreement between the theoretical model and our experimental measurements was observed. Diffusion coefficients of contaminants through swollen polypropylene have an order of magnitude of 10⁻¹¹–10⁻¹⁰ m²/s, which are much more important than those through virgin polypropylene due to the swelling effects. Finally, the effects of pressure and temperature on diffusion coefficients and solubilities were examined and discussed in order to understand the effects of these two chief parameters on the SCCO₂ extraction rate.

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Nomenclature

Symbols

a_s	Surface area of the matrix (m^2)
c	Concentration of solute within the matrix (kg/m^3)
c_f	Concentration of solute in the fluid (kg/m^3)
c_0	Initial concentration of solute within the matrix (kg/m^3)
D	Diffusion coefficient of the solute in the polymeric matrix (m^2/s)
D_0	Constant related to the entropy of activation (m^2/s)
E_a	Activation energy for diffusion (J/mol)
E_d	Contribution of dispersion forces to the cohesive energy (J/mol)
E_h	Contribution of the hydrogen bonding forces to the cohesive energy (J/mol)
E_p	Contribution of the polar forces to the cohesive energy (J/mol)
F	Volume flow rate of fluid (m^3/s)
K	Constant (m^3/kg)
$m(t)$	Mass of solute in the matrix at time t (kg)
m_0	Initial mass of solute in the matrix (kg)
n	Integer
M_w	Contaminant molecular weight (g/mol)
P	Pressure (bar)
P_c	Critical pressure of CO_2 (73.8 bar)
r	Radius of the sphere (m)
R	Gas constant ($8.314 J/(mol K)$)
S	Contaminant solubility in $SCCO_2$ (kg/m^3)
t	Extraction time (s)
T	Temperature ($^{\circ}C$)
T_{ref}	Reference temperature ($25^{\circ}C$)
V_{cont}	Molar volume of the contaminant (cm^3/mol)
V_{CO_2}	Molar volume of CO_2 (cm^3/mol)
V_{mat}	Volume of the matrix (m^3)
V_{ref}	Reference molar volume of CO_2 ($39.13 cm^3/mol$)
Y	Extraction yield (%)

Greek letters

δ_{cont}	Solubility parameter of contaminant ($MPa^{1/2}$)
δ_{CO_2}	Solubility parameter of CO_2 ($MPa^{1/2}$)
δ_d	Contribution of dispersion forces to the solubility parameter ($MPa^{1/2}$)
δ_{dref}	Reference value of dispersion component ($15.6 MPa^{1/2}$)
δ_h	Contribution of hydrogen bonding to the solubility parameter ($MPa^{1/2}$)
δ_{href}	Reference value of hydrogen bonding component ($5.8 MPa^{1/2}$)
δ_p	Contribution of polar forces to the solubility parameter ($MPa^{1/2}$)
δ_{pref}	Reference value of polar component ($5.2 MPa^{1/2}$)
ρ_{cont}	Density of contaminant (g/cm^3)
ρ_{CO_2}	Density of CO_2 (g/cm^3)
ρ_{eb}	Density of the liquid at its normal boiling point (g/cm^3)

ρ_r	Reduced density of CO_2 (g/cm^3)
χ_{12}	Flory–Huggins interaction parameter

is not yet possible. Indeed, during their shelf life, polyolefins can adsorb a wide range of contaminants from their surroundings due to their permeability (Moller et al., 2008). These adsorbed contaminants might be released after that from recycled packaging and migrate into the foodstuffs to contaminate it (Dole et al., 2006a; Stoffers et al., 2005; Moskovkin, 2002; Lawson et al., 1996). This possible contamination strongly limits the recyclability of post-consumer polyolefins as recycled food contact material due to the European Commission regulation related to food contact materials (Commission Regulation (EU), 2014). So, the recycling of post-consumer polyolefins into food contact applications requires high purity materials and therefore rigorous decontamination levels.

Conventional separation techniques such as organic solvent extraction cannot be used to decontaminate recycled polyolefins and provide high purity materials suitable to food contact. These classical techniques exhibit several drawbacks; mainly the fact that they leach a residual amount (traces) of organic solvents in the final product and that it is difficult to handle noxious organic solvent in terms of safety and waste processing, especially on an industrial scale. Furthermore, after extraction process, it is difficult to separate contaminants from the solvent, leading to an expensive posterior handling for the regeneration of solvent (Boutin et al., 2011). Supercritical fluid extraction using carbon dioxide, as environmentally friendly technology aiming at the replacement of classical organic solvent extraction, is a promising and potential technique to decontaminate post-consumer polyolefins and produce clean materials able to be recycled into food contact applications. It presents several advantages compared to traditional extraction methods, related to the supercritical CO_2 features (Jafari Nejad et al., 2010; Hozhabr et al., 2014). $SCCO_2$ has been attracting widespread interest owing to their well-known properties: it has liquid-like density which exhibits good dissolving properties comparable to that of organic solvents, gas-like viscosities, negligible surface tension, and advantageous diffusion properties between those of gases and liquids, leading to an improvement of mass transfer and therefore better extraction in terms of efficiency and speed (Vaz et al., 2013). Furthermore, the ability to tune its solvent power by changing pressure and/or temperature is undoubtedly an important characteristic (Sapkale et al., 2010a).

Within the last decades, $SCCO_2$ has been widely employed for the extraction of polymeric matrices. $SCCO_2$ extraction is becoming an important tool in analytical applications in the polymer area and has seen much attention and rapid development in the last few years. Several research activities on $SCCO_2$ extraction of different polymeric matrices have been published, for example, the extraction of additives from polystyrene (Smith and Taylor, 2002), the extraction of citrates and benzoates plasticizers from poly(vinyl chloride) (Guerra et al., 2002), the quantitative analysis of additives in polypropylene (Thilen and Shishoo, 2000) and polyethylene (Zhou et al., 1999) using $SCCO_2$ extraction.

Modeling and simulation are the fundamental tools for the prediction for dynamic and equilibrium behavior (Lito et al., 2013; Mesbah et al., 2014; Stubbs, 2011; Sakabe et al., 2014), optimization of operating conditions (Bimokr et al., 2012; Jafari Nejad et al., 2011; Wang et al., 2008; da Silva et al., 2015; Desai et al., 2014), and scaling up for the design of industrial extraction processes and the evaluation of their costs (Taher et al., 2014; Lu et al., 2012; de Melo et al., 2014). In this context, the $SCCO_2$ extraction modeling is essential and theoretical models are highly desirable for this purpose (Crank, 1980; Brunner, 1984; Pawliszyn, 1993; Oliveira et al., 2011).

Real supercritical fluid extraction mechanism is generally complex but it may be theoretically described by two essential steps which may limit the rate of extraction, mainly in the extraction of polymeric materials (Sapkale et al., 2010a). These steps are the solubility of solutes in

1. Introduction

Up to now, the recycling of post-consumer polyolefins (polypropylene and polyethylene) into food contact applications (i.e., packaging)

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