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Investigation the effect of super hydrophobic titania nanoparticles on the mass transfer performance of single drop liquid-liquid extraction process

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ABSTRACT

Hydrophobic titania nanoparticles were synthesized by a novel in situ sol-gel method and applied in a single drop liquid-liquid extraction column to enhance the overall dispersed-phase mass transfer coefficient (K_{od}). The chemical system of toluene, acetic acid and water was used, and the direction of solute (acetic acid) mass transfer was from dispersed phase, including: toluene and acetic acid to the continuous phase of water. For such system, much of the mass transfer resistance exists in the dispersed phase, which is nonpolar organic liquid. Hence, modified titania nanoparticles (MTNP's), prepared by sol-gel route, in five different concentrations of 0.001–0.005 wt.% were added in the dispersed phase. Also, the impact of MTNP's at the different solute concentrations and nozzles was investigated. Results indicated an anomalous enhancement in the overall dispersed-phase mass transfer coefficient at 0.002 wt.% of MTNP's. A maximum enhancement of 70% in the overall mass transfer coefficient was found in droplets formed from a nozzle of 2.5 mm inner diameter, containing 3 wt.% of solute. Eventually, based on the theoretical model of Newman, a semi-empirical model was presented, that is capable to predict the overall dispersed-phase mass transfer coefficient of nanofluids with an average absolute relative error of 8.6%.

1. Introduction

Fluids which contain well-dispersed particles with an average size of less than 100 nm, are called nanofluids [1]. Recently, effects of their presence on the transfer phenomena such as heat and mass transfer have been attracted great attention [2]. Once, the improvement of both conductive and convective heat transfer due to the use of nanoparticles was shown [3–6]. Similarity between heat and mass transfer has caused a stimulus for investigating the effect of nanoparticles in the mass transfer operation. Several works have been done on the systems which dealing with the gas and liquid phase, and various improvement effects have been seen due to use of the nanoparticles. Whereas, in case of liquid-liquid extraction process fewer studies have been coducted [2], that have reported increase in the mass transfer coefficients of nanofluids. Bahmanyar et al. [7], used kerosene based SiO_2 nanofluids in a pulsed liquid–liquid extraction column (PLLEC). Their chemical system was kerosene, acetic acid (solute) and water and solute mass transfer was from the kerosene to the water. Based on the pulsation intensity and the nanoparticles concentration, an increase of 4–60% was found in their work. Saien and Bamdadi [8], investigated the effect of Fe_3O_4 and Al_2O_3 nanoparticles in a single drop liquid-liquid extraction column. In their study chemical system was toluene-acetic acid (solute)-water, at the nanoparticles concentration of 0.002 wt.%, the enhancement of solute transfer from dispersed nanofluids (toluene + nanoparticles) was 157% and 121% for magnetite and alumina nanoparticles, respectively. Mirzazadeh Ghanadi et al. [9], used carbon nanotube, ZnO and TiO_2 nanoparticles with different concentration in the water, and investigated mass transfer of succinic acid from *n*-butanol (dispersed phase) to water. They found that, nanoparticles can play a role as a mass transfer promoter in the laminar flow regime of the dispersed phase. Nematbakhsh and Rahbar-Kelishami [10], studied the effect of hydrophobic SiO_2 nanoparticles with different particle size of 10, 30 and 80 nm in an irregular packed column with the chemical system of toluene-acetic acid-water. They used various concentrations of those nanoparticles in water, and found that the maximum enhancement in the

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Nomenclature

d_p	nanoparticle size (nm)
C	solute concentration (mol/m^3)
C^*	equilibrium concentration of solute in dispersed phase (mol/m3)
V	total volume of 200 dropts (m^3)
K_{od}	overall dispersed mass transfer coefficient ($\mu m/s$)
k	local mass transfer coefficient
d	droplet diameter (m)
de	equivalent diameter of drop (m)
dei	equivalent diameter of drop of ith drop (m)
t	contact time (s)
E	extraction fraction
V_t	terminal velocity (m/s)
V_{np}	velocity of nanoparticles (m/s)
K_B	Boltzmann constant, =1.3807 $\times$ 10^{-23} J/K
R	enhancement factor, dimensionless
D_d	molecular diffusivity (m^2/s)
D_{oe}	effective molecular diffusivity (m^2/s)
Re	drop Reynolds dimensionless number
Re_{nf}	nanofluid Reynolds dimensionless number
n_i	number of droplets with d_{ei}
E_1	ratio of the major to the minor axis of the oblate spheroid
C_D	drag coefficient, dimensionless
S_{os}	area of an oblate spheroid (m^2)
S_s	area of a sphere which has equal volume of an oblate spheroid (m^2)
g	gravity, (m/s^2)

Greek symbols

μ	dynamic viscosity (Pa s)
ρ	density (kg/m^3)
γ	interfacial tension (N/m)
ν	kinematic viscosity (m^2/s)
Φ	volume fraction

Subscripts

0	initial point
nf	nanofluid
np	nanoparticles
c	continuous phase
d	dispersed phase

overall mass transfer coefficient was 42% in 0.05 vol% of the smallest nanoparticles. Ashrafmansouri and Nasr Esfahany [11], investigated the effect of toluene based SiO_2 nanofluids on the mass transfer and hydrodynamics characteristics of a spray liquid-liquid extraction column. They observed that, nanofluids have not any sensible effect on the hydrodynamic performance of toluene-acetic acid-water system. However, in 0.001 vol% of that nanoparticles a maximum enhancement of 47% in the overall mass transfer coefficient was detected. Recently, Goodarzi and Nasr Esfahany [12], investigated the effects of the hydrophilic SiO_2 nanoparticles in the aqueous phase of toluene-acetic acid-water systems. They reported that when toluene and acetic acid are the dispersed phase, using SiO_2 nanoparticles in the water couldn't enhance the mass transfer rate, even at the concentration of 0.1 vol% of that nanoparticles the overall dispersed phase mass transfer reduced up to 22% in their work. In all the studies in this field, microconvection created due to the Brownian motion of nanoparticles is the most reported possible reason for the anomalous enhancement of mass transfer rate [7–14]. So, it can be more efficient if the nanoparticles would be used in the phase with higher mass transfer resistance. In this investigation, a single drop liquid-liquid extractor as a simple study column, which provides easy and accurate control over the main specification of the extraction process, was chosen and we have focused on the toluene, acetic (solute) and water chemical systems. Solute transfer was from the toluene as the dispersed phase to the water as the continuous phase. In this system major resistance of the mass transfer exists in the dispersed phase [11,12], so nanoparticles should have a good distribution in the toluene. To this end, titania (TiO_2) nanoparticles, which has not been used in the dispersed phase, have synthesized and then functionalized through an in situ sol-gel method with using of a silane coupling agent. Aside the titania nanoparticles concentration, the effect of solute concentration and nozzle tip size on the mass transfer performance of the single drop experiments has been investigated. At the end of this work, with modification of the Newman model by experimental data, a semi-empirical model has been proposed for predicting the overall dispersed-phase mass transfer coefficient.

2. Experimental

2.1. Materials

Toluene and acetic acid with purity above 99.9% were purchased from Merck and ultrapure deionized water was prepared, these materials were used as the chemical extraction systems. To synthesis hydrophobic titania nanoparticles, ultrapure isopropyl alcohol, tetraethyl orthotitanate (purity higher than 95%), citric acid and ammonium hydroxide (25% NH4OH), all supplied from Merck, were used. For surface modifying of nanoparticles, trimethoxi (octyl) silane (octyltrimethoxysilane) with a purity of 96% was prepared from Aldrich.

2.2. Synthesis of super hydrophobic TiO_2 nanoparticle

Titanium dioxide (TiO_2) due to its unusual structural, optical, electronic, magnetic and chemical properties, exhibits wide applications in pigments, UV protection creams, photo-catalysis, solar cells, water and air purification [15–17]. There are some different methods for synthesis of titania nanoparticles such as chemical precipitation, microemulsion, hydrothermal and sol-gel, which among them, sol-gel method is the most preferred procedure to synthesis titania nanoparticles [18]. There would be hydroxyl bonds on the titania nanoparticles synthesized through sol-gel method [19], which makes them as hydrophilic materials with no inclination to distribute in non-polar organic phase [20]. Although TiO_2 nanoparticles due to high surface area to volume, have peculiar properties and advantage to bulk or micro sized particles [16], but for the same reason they tend to agglomerate [20,21]. In order to change the nanoparticles hydrophobicity and to prevent them from agglomeration, various methods have been used. Surface chemical modification with organic molecules can be utilized to stabilize nanoparticles efficiently in organic solution [21]. Surface treatment of nanoparticles can be performed during or after the synthesis process, the former one is more time and cost effective, so in this work they have been synthesized and functionalized during an in situ method. Silane coupling agents typically