Reactive & Functional Polymers 73 (2013) 595–605

Contents lists available at SciVerse ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

Resin screening for the removal of pyridine-derivatives from waste-water by solvent impregnated resin technology

J. Bokhove [a,*], B. Schuur [b], A.B. de Haan [a]

[a] Eindhoven University of Technology, Process Systems Engineering Group, Department of Chemical Engineering and Chemistry, PO Box 513, 5600 MB Eindhoven, The Netherlands
[b] University of Twente, Faculty of Science and Technology, Sustainable Process Technology Group, Green Energy Initiative, PO Box 217, 7500 AE Enschede, The Netherlands

ARTICLE INFO

Article history:
Received 26 September 2012
Received in revised form 11 December 2012
Accepted 16 December 2012
Available online 5 January 2013

Keywords:
Solvent impregnated resin
4-Cyanopyridine
4-Nonylphenol
Resin screening
Mass-transfer
Equilibrium extraction

ABSTRACT

The selective removal of pyridine derivatives by solvent impregnated resins has been studied. A solvent impregnated resin consists of a macro-porous particle that is impregnated with a solvent. This technology allows the use liquid–liquid extraction in fixed-bed operation, and prevents problems like entrainment and irreversible emulsification. 4-Cyanopyridine was chosen as model pyridine derivative, and 4-nonylphenol was used as solvent. The aim of this study was to select the most suitable resin for this application. While in the literature there are mainly two types of resins used, MPP and Amberlite XAD type, a comparative study has not yet been conducted. In this study, a series of resins were impregnated with the solvent and applied in sorption experiments to study on the effect of the resin properties on the capacity, selectivity and mass-transfer rates of the solvent impregnated resins. It was found that the capacity could be estimated accurately with the previously developed liquid–liquid extraction equilibrium model. Additionally, the selectivity was determined by the solvent properties, and hardly affected by the resin matrix. The mass-transfer rates were primarily determined the by particle diameter, whereas the effect of the porosity is small. On the basis of the results it was established that Amberlite XAD4 had the best combination of capacity, mass-transfer rate, mechanical strength, selectivity and pressure drop over a fixed-bed column and was therefore chosen for a more detailed study. The results showed that the breakthrough curve is broad due to mass-transfer limitations. The loading cycle of the column could be described with great accuracy using the mathematical model developed in this study. Regeneration of the column could be performed efficiently with a pH-swing using hydrochloric acid at a pH of 1. The fixed bed column was percolated with 7000 bed volumes of aqueous solutions varying in composition. No reduction in the capacity was observed which demonstrated that the SIR consisting of Amberlite XAD4 and 4-nonylphenol is highly stable.

1. Introduction

Trace removal concerns the removal of impurities at low concentrations, for example from product streams to meet the desired product specifications, or from waste-streams to prevent emissions of toxic compounds. Industrial processes where by-products are formed with a high solubility in water may result in wastewater streams that are complex of nature and difficult to treat by conventional technologies. The work in this paper is focused on an aqueous waste-stream containing aromatic nitrogen species such as pyridine and pyridine derivatives. These types of streams are formed in for example the production of bulk chemicals such as acrylonitrile, pyridine and cyanopyridine [1–4], and the components have a relatively high solubility in water. Without precautions they might end up in the waste-water stream. Due to the toxicity and poor biodegradability of some of these components, the treatment of such wastewater streams is pursued, being of great environmental importance. Besides the pyridine derivatives, other components are present such as oxygenated species as acrylic acid and acetic acid [1]. The flow rate of the waste-stream produced ranges from 30 to 50 m^3/h [1]. The aim of this study is to selectively recover the pyridine derivatives from this stream prior to biological wastewater treatment, which will make the treatment easier.

In our previous studies we proposed solvent impregnated resins (SIRs) as a promising technology for the removal of pyridine derivatives from the stream prior to further treatment, and developed a solvent [5] with a high capacity and selectivity towards 4-cyanopyridine. A SIR consists of a macro-porous resin in which a solvent is immobilized [6]. The solvent is retained inside the porous particle by a combination of a high affinity for the resin and its low solubility in the aqueous phase. This technology combines the

* Corresponding author. Tel.: +31 40 247 2840; fax: +31 40 246 3966.
E-mail addresses: j.bokhove@tue.nl (J. Bokhove), b.schuur@utwente.nl (B. Schuur).

1381-5148/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.reactfunctpolym.2012.12.011

Nomenclature

Abbreviations

CP	4-cyanopyridine
NP	nonylphenol
SIR	solvent impregnated resin
Re	Reynolds number
LDF	linear driving force

Symbols

A	surface area (m^2)
CF	capacity factor (L/kg)
D_{ax}	axial dispersion coefficient (m^2/s)
D	diffusivity (m^2/s)
D_{Eff}	effective diffusivity (m^2/s)
d_c	column diameter (m)
d_p	resin diameter (m)
f_m	friction factor (–)
K	equilibrium constant (–)
K_{LDF}	overall mass transfer coefficient (/s)
k_f	aqueous phase mass transfer resistance (m/s)
L	length (m)
M	mass (kg)
m	partitioning coefficient (–)
N	number of moles (mole)
Δp	pressure drop (Pa)
Q_v	volumetric flow rate (m^3/h)
q	SIR loading (g/kg SIR)
S	selectivity (–)
u	interstitial velocity (m/s)
V_{Bed}	volume of the fixed bed (m^3)
$v_{m,0}$	fluid superficial mass velocity (kg/m^2 s)
$\overline{X}$	molar fraction in the organic phase (mole/mole)
x	molar fraction in the aqueous phase (mole/mole)
z	axial position in the fixed-bed column (m)

Greek symbols

ρ	density (kg/m^3)
μ	viscosity (Pa s)
ε_b	bed porosity (–)
ϕ	tortuosity (–)

Subscripts

i	length of a 4-nonylphenol oligomer complexed with the cyanide group
j	length of a 4-nonylphenol oligomer complexed with the pyridine nitrogen
h	length of a 4-nonylphenol oligomer
aq	aqueous phase
org	organic phase
ini	initial
eq	equilibrium
SA	self-association
c	complexation

Superscripts

N	pyridine nitrogen
$C\equiv N$	cyanide nitrogen

advantages of adsorption and liquid–liquid extraction in a single unit-operation. The advantage of liquid–liquid extraction is that by aiming at specific interactions both a high capacity and selectivity can be obtained. However, the disadvantage is that by entrainment and irreversible emulsification, solvent is lost to the aqueous phase which is undesired, especially in the case of trace-removal, because a new trace is added. The advantage of adsorption is the use of fixed bed operation, in which a high number of theoretical stages can be achieved, allowing for difficult separations including trace removal. However, the regeneration of typical adsorbents such as activated carbon can be difficult due to the non-specific and strong interactions between solute and adsorbent. In SIR technology, the advantages of liquid–liquid extraction and adsorption are combined, making it possible to reach high capacities, high selectivities and allowing the use of a fixed bed operation that prevents problems like entrainment and irreversible emulsification. In comparison with adsorption on activated carbon, the energy requirements in the regeneration may be reduced when the binding strength between the solvent and solute are sufficiently weak. A key parameter in SIR technology is leaching of the solvent to the aqueous phase, resulting in a capacity reduction over time. For this reason, a solvent with a very low solubility in water, and a resin with a high affinity for the solvent are required. In our previous study we showed that phenol based solvents have a high capacity and selectivity towards 4-cyanopyridine in presence of acetic acid [5]. Additionally, the phenols have a very low solubility in water, e.g. 5 ppm for 4-nonylphenol [7]. This makes this class of solvents a good candidate to use in SIR technology for the removal of aromatic nitrogen species from wastewater streams that also contain organic acids.

Besides the solvent also a resin needs to be selected, in the literature the most frequently used resins are macro-porous propylene (MPP) [8–10] and Amberlite XAD type resins [11–16]. MPP is used in the commercially applied MPPE process for the removal of hydrocarbons from waste-water in off-shore applications [17]. The main advantages of MPP are the low cost, high porosity and high mechanical strength. A process was developed for the removal of phenol and metyl-*tert*-butylether from water using MPP impregnated with a phosphine oxide and phenol based solvent [9,10]. However, a drawback of MPP is its large particle diameter of 1 mm, which may result in slow mass-transfer in the case of more viscous solvents (e.g. 4-nonylphenol). Amberlite XAD type resins are often used because of their high porosity, however a comparative study on the performance of this resin in reference to other resins has not yet been conducted. The aim of this study is therefore to compare different types of resins and study the effect of resin matrix, diameter and pore size on the process parameters like capacity, selectivity and mass-transfer rates. On the basis of experimental data a model was developed and used for process evaluation in order to make the final selection of the resin that was evaluated in fixed bed column experiments. For this study, we used 4-nonylphenol (NP) as solvent and 4-cyanopyridine (CP) as solute, because the thermodynamic equilibrium model of CP extraction by NP was extensively studied [18].

2. Theory and approach

2.1. Approach

In a SIR, the solvent is impregnated in the pores of the resin particles. The maximum capacity of resins corresponds to the volume of solvent that is impregnated, i.e. to the porosity. The capacity is not the only factor of importance, also the resin stability and the rate of mass transfer are key parameters in a SIR-process. These factors are determined mainly by the functionality, the particle size, porosity and pore diameter of the particles. To investigate