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Selective recovery of a pyridine derivative from an aqueous waste stream containing acetic acid and succinonitrile with solvent impregnated resins

J. Bokhove [a], T.J. Visser [b], B. Schuur [c,*], A.B. de Haan [d]

[a] Eindhoven University of Technology, Process Systems Engineering Group, Department of Chemical Engineering and Chemistry, PO Box 513, 5600 MB Eindhoven, The Netherlands
[b] Syncom B.V. Kadijk 3, 9747 AT Groningen, The Netherlands
[c] University of Twente, Faculty of Science and Technology, Sustainable Process Technology Group, Green Energy Initiative, PO Box 217, 7500 AE Enschede, The Netherlands
[d] Faculty of Applied Sciences, Department of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

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ABSTRACT

Solvent impregnated resins (SIRs) were evaluated for the recovery of pyridine derivatives from an aqueous waste-stream containing also acetic acid and succinonitrile. For this purpose, a new solvent was developed, synthesized and impregnated in Amberlite XAD4. Sorption studies were used to determine the capacity, selectivity and the mass-transfer rate. A high capacity of 21 g 4-cyanopyridine (CP) per kg SIR was found, with very high selectivity toward CP over the other solutes of at least 570. A modified Langmuir equation could describe the equilibrium sorption isotherm. Both the linear driving force model and a Fickian diffusion model were evaluated. The Fick-model described both regeneration and loading best. The CP-diffusivity through the solvent phase was estimated at $6.53 \cdot 10^{-13} \pm 2.5\%$ $m^2\ s^{-1}$. The model was validated using fixed-bed column experiments. The R^2 values for this model ranged between 0.94 at a flow rate of 5 mL/min and 0.99 at a flow rate of 1 mL/min during the loading cycle. Due to mass-transfer limitations the breakthrough profiles were broad and breakthrough occurred after 5 or 23 bed volumes, for flow rates of 5 and 1 mL/min, respectively. Both acetic acid and succinonitrile broke through immediately due to the very high CP-selectivity of the SIR.

1. Introduction

Trace removal involves the removal of impurities present in low concentrations from either waste-streams or product streams, and aims at preventing emission of toxic compounds or at product purification. The main issue in trace-removal is the high number of separation stages that are required to achieve the desired trace-compound(s) removal from the product stream. Typically outlet concentrations below 5 ppm are desired and especially when large streams are to be purified, this could lead to large equipment if the separation is less efficient. Novel, highly efficient technologies are thus desired, and because traditional separation technologies like adsorption [1] and extraction [2] can both yield high capacities and selectivities, they suffer from drawbacks like difficult regeneration in the case of adsorption, and entrainment or irreversible emulsification in the case of extraction.

In this study, a promising alternative for these technologies, the solvent impregnated resin (SIR) [3] was evaluated for a specific case of wastewater treatment. The wastewater stream that is considered in this work consists of pyridine derivatives (e.g. 4-cyanopyridine, CP), nitriles (e.g. succinonitrile) and oxygenated compounds (e.g. acetic acid) that are typically formed in the production of cyanopyridine, acrylonitrile and pyridine [4–7]. The aim was to selectively remove the highly water soluble pyridine derivatives from this stream, since without precautions there is a chance that they might end up in the wastewater stream, resulting in highly diluted aqueous waste streams that are complex of nature. Due to the toxicity and poor biodegradability of some of these components, the treatment of such wastewater streams is of great environmental importance [4–7].

Using a SIR-based process [3,8] for water purification is beneficial, because the solvent is immobilized in a macro-porous particle, and as a result, mixing and settling of the aqueous and organic phase are no longer required and entrainment and irreversible emulsification are prevented. In the literature, SIRs have been developed for the in-situ recovery of products from a fermentation

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* Corresponding author.
E-mail addresses: Jeroen.Bokhove@gmail.com (J. Bokhove), t.visser@syncom.nl (T.J. Visser), b.schuur@utwente.nl (B. Schuur).

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Nomenclature

Abbreviations

CP	4-cyanopyridine
$(CP)_nDBP$	complex of 4-cyanopyridine with the reactive solvent
CPH^+	protonated 4-cyanopyridine
DMF	dimethylformamide
DMS	dimethylsulfate
HAc	acetic acid
H^+	proton
LDA	lithium diisopropylamide
DBP	the reactive brominated phenol solvent
SIR	solvent impregnated resin
SN	succinonitrile
Re	Reynolds

Symbols

A	cross-sectional area of the column [m^2]
c	concentration [g m^{-3}]
CF	capacity factor [L/g]
D	effective diffusion coefficient [m^2 s^{-1}]
D_{ax}	axial dispersion coefficient [m^2 s^{-1}]
d_p	diameter of the SIR [m]
ε_b	void fraction in the bed [–]
ε_p	void fraction in the resin [–]
K_c^{app}	apparent complexation strength [(L mole^{-1})$^{1-n}$]
K_a	dissociation constant [L mole^{-1}]
k_f	aqueous phase resistance toward mass-transfer [s^{-1}]
K_{LDF}	overall mass-transfer coefficient [s^{-1}]
K_D	distribution coefficient [–]
L	length of the column [m]
$M_{w,cp}$	molecular weight of 4-cyanopyridine [g mole^{-1}]
n	stoichiometry [–]
q	loading of the SIR [g CP/kg SIR]
$q_{s,tot}$	solvent loading of the SIR [mL solvent/kg SIR]
R	radius of the SIR [m]
r	radial position [m]
S	selectivity [–]
t	time [s]
u	interstitial velocity [m/s]
V	volume [m^3]
z	normalized position in the bed [–]

Subscripts

eq	equilibrium
org	organic phase
aq	aqueous phase
bt	breakthrough

superscript

t	time

broth [9], the recovery of caprolactam from water [10] and the removal of several other polar organic compounds from water [11–17]. The drawback of this technology is that leaching of solvent may result in a fast depletion of the capacity [18], which should be minimized by selecting a solvent with a low solubility in water and a high affinity for the resin.

In our previous study a solvent selection procedure was presented for the selective removal of CP from an aqueous phase [19]. In that study, it was found that with phenol based solvents the highest capacities were obtained, whereas 4-nonylphenol has a very low solubility (5 ppm) [20] in the aqueous phase, which is beneficial for SIR processes. By impregnating 4-nonylphenol in Amberlite XAD4, a resin consisting of polystyrene cross-linked with divinylbenzene, a highly stable SIR was obtained [21]. The regeneration could be performed by a pH-swing with hydrochloric acid at a pH of 1, where the concentration of CP could be increased from 0.5 g/L in the loading cycle as feed solution to a maximum of 3 g/L in the effluent during the regeneration cycle. However, the capacity of the SIR containing 4-nonylphenol was limited, and for this reason a modified phenol with a higher capacity for the target compound was developed and custom-synthesized. The designed solvent, consisting of a 1:1 mixture (mole basis) of 3,5-dibromo-4-(4,6,6-trimethylheptyl)phenol and 3,5,-dibromo-4-(4,8-dimethylnonyl)phenol is presented in Fig. 1. The solvent (abbreviated by DBP) is a mixture of two molecules varying in their alkyl chain to reduce the viscosity.

After validating the high capacity of 43 g CP/kg SIR [19], the aim of the here presented study was to characterize the performance of a SIR consisting of Amberlite XAD4 resins impregnated with the brominated solvent for the selective recovery of CP from a mixture of acetic acid (HAc) and succinonitrile (SN), the molecular structures of the solutes are given in Fig. 2.

Elements of the study to characterize the performance of the SIR include the development of a thermodynamic model to describe the capacity, a mass-transfer model to evaluate the mass-transfer rate and a fixed bed model to evaluate the breakthrough profiles during the loading of a column and the effluent concentration during the regeneration of the column. The models were validated with experimental fixed-bed column data. Finally, the evaluated model was used to perform process-simulations to determine the

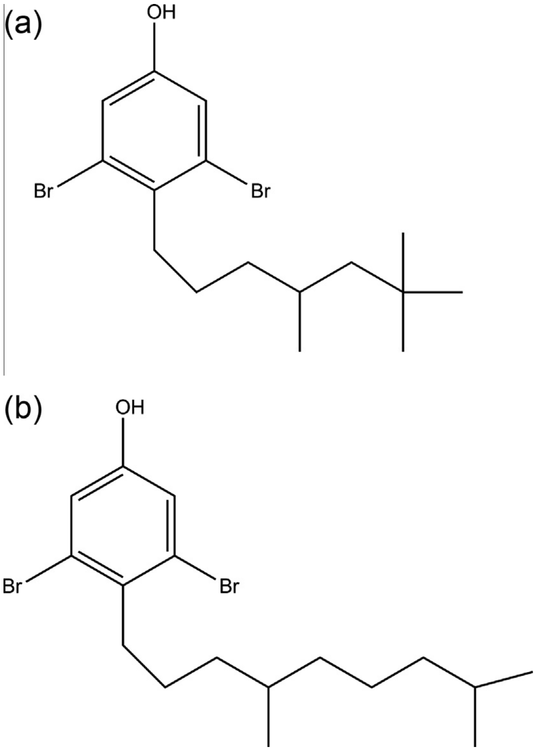

Fig. 1. Molecular structure of the solvent, consisting of a 1:1 mixture of two alkylated dibromophenols.