Parameter study on the adsorptive drying of isopropanol in a fixed bed adsorber

Bernd Burrichter [a,*], Christoph Pasel [a], Michael Luckas [a], Dieter Bathen [a,b]

[a] Thermal Process Engineering, University of Duisburg-Essen, Lotharstraße 1, D-47057 Duisburg, Germany
[b] Institute for Energy and, Environmental Technology e.V. (IUTA), Bliersheimer Str. 60, D-47229 Duisburg, Germany

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ABSTRACT

This work focuses on the influence of process parameters on the dynamics of adsorptive water removal from polar organic solvents in a fixed bed adsorber. As a model solvent isopropanol with water concentrations between 5 and 4000 ppm$_w$ was used. In a first step equilibrium loadings on 3A and 4A zeolites were determined by shaker bottle experiments. The results were fitted to the Langmuir equation. In a second step fixed bed experiments were carried out in order to characterize the dynamic behavior of the adsorption process. In these experiments 3A zeolite shows a better drying performance than 4A zeolite. The breakthrough curves (BTC) could be well described by dynamic simulations using a set of differential equations for the mass balances and a linear driving force approach (LDF) for the kinetics. Pore diffusivities in the order of 10^{-12} m^2/s were obtained by the simulation, indicating that surface diffusion in the pores of the zeolites is the predominant mechanism of mass transfer.

1. Introduction

Processing industry faces an increasing demand of very pure organic solvents. Especially the water content is a critical factor in industrial processes. Water may e.g. cause undesired side reactions or catalyst poisoning; in these cases it should be almost completely removed. Adsorptive water removal on zeolites, silica gels and aluminas is the method of choice used in industrial applications to reach water contents below 20 ppm. In spite of this, there are only a few systematic investigations on liquid phase adsorption. Additionally all published work [1–17] either deals with very dry non-polar solvents (e.g. benzene, toluene or cyclohexane) or with polar solvents (e.g. alcohols), which are dried to water contents in the percent range. Up to now there is no detailed investigation on the adsorptive water removal from hydrophilic solvents in the ppm-region.

Burfield et al. describe the correlation between different properties of the solvent and the minimum residual water content. Solvents with a high relative permittivity, which are completely miscible with water, are more difficult to dry than non-polar solvents. This is shown by multiple experiments with toluene, ben-

zene, ethyl ether, dichloromethane, different amines and various alcohols. The authors tested different adsorbents, but molecular sieves (type A) were in almost every case the desiccant of choice [1–4].

Several research groups investigated the adsorptive drying of ethanol due to high investment and energy costs of alternative processes like azeotropic distillation [5–8]. A comprehensive study on the dehydration of ethanol on 3A zeolites has been published by Teo and Ruthven in 1986. In batch kinetic and fixed bed experiments different mass transfer resistances were analyzed and additionally a theoretical model was developed to predict breakthrough curves in a fixed bed adsorber. Teo and Ruthven worked out that the intraparticle diffusion is the main resistance to mass transfer, whilst diffusion through the surrounding film of the particle is secondary. Diffusion coefficients in the pores of 6.0×10^{-10} m^2/s were found [9]. Yamamoto et al. report their findings about ethanol dehydration by five different molecular sieves. 13X zeolite showed the highest water capacity. Analysis of the breakthrough curves results in intraparticle diffusion coefficients of 4.9×10^{-12} to 1.3×10^{-11} m^2/s, whereby the diffusivities were proportional to the pore diameter of the synthetic zeolites [10]. Further work deals with water removal from other polar solvents, like 1- or 2-propanol. Besides experimental results, diffusion coefficients were published in the range of 8.51×10^{-9} m^2/s down to 4×10^{-17} m^2/s [11,12]. All studies on alcohol dehydration were carried out in a concentration range between 0.1 and 10 wt% (1000 ppm$_w$–100.000 ppm$_w$); dynamic experiments to determine

* Corresponding author. Tel.: +49 203 379 1731; fax: +49 203 379 3119.
E-mail addresses: bernd.burrichter@uni-due.de (B. Burrichter), christoph.pasel@uni-due.de (C. Pasel), michael.luckas@uni-due.de (M. Luckas), dieter.bathen@uni-due.de (D. Bathen).

Nomenclature

b	parameter of the Langmuir equation, –	q_{mon}	monomolecular loading, $g_{H2O}/g_{adsorbent}$
c_i	concentration, $mg_{H2O}/kg_{solution}$	T	temperature, K
$c_{i,0}$	inlet concentration, $mg_{H2O}/kg_{solution}$	t	time, s
$c_{i,eq}$	equilibrium concentration, $mg_{H2O}/kg_{solution}$	u_{LR}	superficial velocity, m/s
D_{12}	molecular diffusion coefficient, m^2/s	v_A	specific molecular volume of solute (A), cm^3/mol
D_{AX}	axial dispersion coefficient, m^2/s	v_B	specific molecular volume of solvent (B), cm^3/mol
d_p	bead size of the particles, m	$\dot{V}_{solu}$	volume flow of solution, m^3/s
D_{Pore}	diffusion coefficient in the pores, m^2/s	z	axial dimension, m
H	length of the fixed bed, cm	Z	length of the simulation column, cm
k	overall mass transfer coefficient, s^{-1}		
k_f	film mass transfer coefficient, m/s	*Greek symbols*	
K_F	constant of the Freundlich equation, $kg_{solution}/mg_{H2O}$	ε_L	void fraction of the bed, –
m_{ADS}	mass of adsorbent, kg	ε_P	void fraction of the particle, –
m_{solu}	mass of solution, kg	μ_{fluid}	viscosity of the solvent, $kg/(m\,s)^{-1}$
n	exponent of the Freundlich equation, –	$\rho_{Ads,b}$	bulk density of the adsorbent, kg/m^3
p_A	Parachor of solute (A), –	$\rho_{Ads,w}$	skeletal density of the adsorbent, kg/m^3
p_B	Parachor of solvent (B), –	ρ_{fluid}	density of the solvent, kg/m^3
q	loading of the adsorbent, $g_{H2O}/g_{adsorbent}$		
q_{eq}	equilibrium loading of the adsorbent, $g_{H2O}/g_{adsorbent}$		

the kinetic parameters usually start with initial concentrations of several thousand ppm$_w$.

Another area of interest was the drying of hydrophobic solvents like benzene or toluene. Joshi and co-workers study the adsorptive water removal from toluene, benzene and p-xylene using 3A and 4A zeolites. They measured equilibrium data in shaker bottle experiments and determined kinetic parameters, like diffusion coefficients in the pores of the zeolites, on two different ways. On the one hand they carried out batch kinetic experiments in flasks and on the other hand they determined diffusivities by dynamic experiments in a fixed bed adsorber. These experiments could be successfully predicted by varying the pore diffusivity as a fitting parameter in a physical model. Due to the simplicity of the second method, pore diffusivities were determined by this means in most of the following investigations. For the systems examined by Joshi diffusivities were in the range between 4.3–8.28×10^{-9} m^2/s [13,14]. Rivero obtained similar results when investigating the adsorptive dehydration of styrene on activated aluminas [15]. Basmadjian calculated pore diffusivities from published experimental data for different solvents. In most cases diffusion coefficients were in the range 1×10^{-8} to 1×10^{-10} m^2/s, although there were uncertainties due to inconsistencies in the setup of the different experiments [16]. Goto et al. obtained pore diffusivities from batch kinetic experiments for the drying of benzene on activated aluminas in the range of 7×10^{-12} m^2/s [17].

This literature review shows that there is only little data available regarding the adsorptive drying of organic solvents up to now. For this reason the authors of this article systematically investigate the adsorptive water removal from different polar solvents in the trace humidity region on 3A and 4A zeolites. In a first step extensive equilibrium data for the drying of primary and secondary alcohols and acetates was experimentally determined and published [18]. In this paper the results of experiments on the adsorptive drying of organic solvents in a fixed bed adsorber will be presented, whereby isopropanol is used as a model substance.

2. Experimental

2.1. Material and analytics

Desiccants used in this study were 3A and 4A zeolites with a bead size between 1.0 and 2.0 mm supplied by *Zeochem AG* (Ueti-

kon, Switzerland). The basic physical properties are listed in Table 1.

The model solvent isopropanol was of reagent grade and the desired water content was adjusted with ultrapure water, which was given directly to the storage container via a syringe. The determination of the water content in the solvent was executed by a coulometric Karl-Fischer-Titration. By this means accurate and reliable measurements from 5 to 10,000 ppm$_w$ were possible. The accuracy of the analytics was tested periodically with certified water standards. A disadvantage of this offline measurement principle is the necessity to take samples manually.

2.2. Equilibrium experiments

2.2.1. Experimental setup and procedure

Prior to each experiment the zeolites are activated according to the manufacturer's guidelines at 300 °C for at least 18 h. In addition all flasks and caps are heated up to 170 °C to avoid residual water on any surface. Then 0.05–3 g of the adsorbent is placed inside a flask with 40 g of solvent with a defined amount of water. Two flasks in every test series are filled only with solvent as blind samples to detect potential contaminations. All work was carried out in a nitrogen purged glovebox to prevent contamination from atmospheric humidity. After preparation the flasks are put in an incubator shaker under constant conditions (20 °C and 150 rph) until equilibrium is reached. For solvents, which are not extremely viscous, a period of 5–7 days is sufficient for equilibration. When equilibrium is reached, the water content is measured a second time and the loading of the adsorbent is calculated by the equation:

Table 1
Basic physical properties of the adsorbents.

	3A	4A
Commercial name	Zeochem® Z3-01	Zeochem® Z4-01
Pore opening (Å)	3.2	3.8
d_p (mm)	1.0–2.0	1.0–2.0
$\rho_{Ads,b}$ (kg/m³)*	0.70	0.69
ε_L (–)*	0.4	0.4
ε_P (–)	0.55	0.55

* Data refer to an adsorber column with an inner diameter of 16 mm.