

Recovery of benzaldehyde from aqueous streams using extractant impregnated resins

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Abstract

The performance of Extractant Impregnated Resin (EIR) technology for extraction of aldehydes from aqueous solutions has been investigated. The extraction capabilities of several different aliphatic and aromatic primary amines towards aldehydes were tested and compared. Aliphatic amines showed high affinity. The most promising extractant, Primene[®] JM-T, was immobilized in a porous particle. As a solid support three different macroporous adsorbents were tested, XAD-16, MPP and Stamypor. Their capacities for the removal of aldehydes were compared with the non-impregnated resin and the resin impregnated with the non-reactive solvent. It was shown that the addition of a reactive extractant can increase the adsorption capacity of an otherwise poor adsorbent for several orders of magnitude. The capacity for the removal of aldehydes was increased with the increase of amine loading on the particle. Temperature influence on the sorption of benzaldehyde on fully impregnated MPP was studied. It was shown that with temperature increase, sorption capacity is increased. The stability of EIRs regarding the loss of the extractant due to the leakage in water was also studied. It was shown that immobilization reduces the extractant's solubility in water. Sorption kinetics was investigated for fully impregnated XAD-16 and MPP. The modified shrinking core model was used to determine the rate controlling step and it was shown that this sorption is most likely controlled by both chemical reaction and diffusion in the particle.

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1. Introduction

Aqueous solutions containing components present in low concentrations are the result of many industrial processes. Very often it is necessary to

recover them from these streams, either to obtain a valuable product or to prevent contamination of the environment. Therefore, it is desirable to reduce their presence in water to very low concentrations (ppb-level), rendering conventional reactive extraction unfeasible due to the high excess of solvent/reactant required. On the other hand, adsorption is very often not selective enough, has very low capacity or is very expensive when resins containing functional groups are used.

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Nomenclature

Symbols

n	amount of substance, mol
C	concentration, mol/l
K_r	reaction equilibrium constant, l/mol
K_{ph}	physical partitioning ratio
D	overall distribution ratio, defined by Eq. (3)
V	volume, l
t	time, s
q	loading of the particles with benzaldehyde, mol/l
q_{JMT}	loading of the particle with Primene [®] JM-T, mol/l
X	fractional conversion of the EIR at time t , defined by Eq. (7)
X_e	fractional conversion of the outer surface of the EIR, defined by Eq. (8)
K	equilibrium distribution ratio of benzaldehyde between particle and water
a	average radius of the particle, m
δ	thickness of the stagnant liquid film, m
b	stoichiometric coefficient
D_e	effective diffusivity in the resin phase

D_f	diffusivity in the liquid film
K_c	apparent chemical reaction rate constant

Subscripts and superscripts

org	organic
aq	aqueous
Ald	aldehyde
Am	amine
AldAm	complex formed by aldehyde and amine (Schiff base)
o	initial

Component abbreviations

1-PD	1-phenyldodecane
SQ	squalene
MBDIPA	4,4'-methylenebis-(2,6-diiodopropylaniline)
MBIPMA	4,4'-methylenebis-(2-isopropyl-6-methylaniline)
ODA	octadecylamine
DDA	dodecylamine
JM-T	Primene [®] JM-T

As a process that can overcome these disadvantages, but maintain the advantages of both mentioned separation techniques, Extractant Impregnated Resin (EIR) technology is proposed [1]. It is a synergistic combination of adsorption and reactive extraction that combines a high capacity and selectivity with relatively simple equipment and operation. Already a lot of research has been

done in this field for removal of traces of metals from aqueous streams [2–4]. Lately, the EIR technology has been extended for recovery of organic compounds, like phenols [5], flavonoids [6], carboxylic acids [7–10], amino acids [11,12], and antibiotics (spiramycin [13]). In the present research, we investigate the removal of aldehydes from diluted aqueous streams using EIR technology, which has,

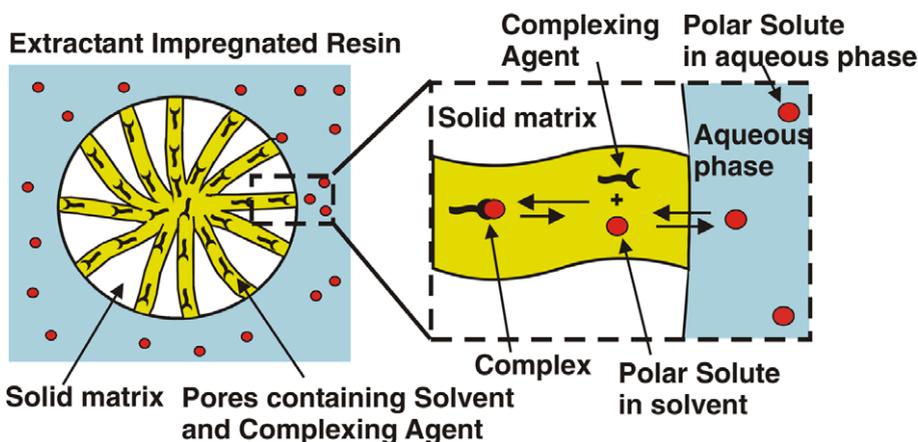


Fig. 1. Extractant impregnated resins.

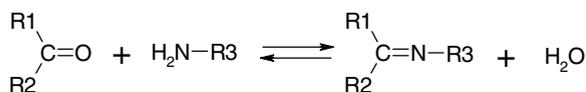


Fig. 2. Schiff base formation.

according to our knowledge, not been done so far. Aldehydes are compounds very often used in chemical and pharmaceutical industry as raw materials and intermediates [14].

The concept of EIRs is based on the incorporation of a selective extractive reagent into a porous particle by physical impregnation. In order to apply this technology for the removal of components from water, it is necessary to fill the pores with a water-insoluble organic phase. However, aldehydes do not show a strong tendency to transfer from an aqueous to an organic phase. To improve their affinity for the organic phase, it is functionalised with a complexing agent capable of forming a complex with aldehydes, which remains in the organic phase (Fig. 1). This reaction should be reversible but sufficiently strong to increase the aldehyde's affinity for the organic phase by several orders of magnitude to obtain an economically feasible process. As complexing agents, primary amines can be used because they form stable Schiff bases in reaction with aldehydes (Fig. 2) [15]. By choosing an amine with a large apolar organic tail, it can be assured that it is insoluble in water, thus preventing potential loss of the extractant.

According to the mentioned criteria, some commercially available aliphatic and aromatic amines

were selected and experimentally tested by liquid–liquid experiments for their affinity towards benzaldehyde. Benzaldehyde was chosen to represent aldehydes due to its commercial and industrial significance, especially as a building block for speciality chemical production [14,16]. The performance of three different polymeric resins, Amberlite XAD-16 (polystyrene-co-divinylbenzene), MPP (macroporous polypropylene) and Stamypor (macroporous polyethylene), was investigated.

Temperature effects on the sorption process were investigated to explore feasibility of temperature shift for the regeneration of these EIRs. The stability of EIRs, regarding the loss of the extractant due to the leakage in water, was also studied. Finally, the kinetics of the EIR process was investigated. In order to determine the rate controlling step, the modified shrinking core model was applied.

2. Experimental

2.1. Reagents

Benzaldehyde, 1-phenyldodecane (1-PD), squalene (SQ), dodecylamine (DDA), octadecylamine (ODA), *n*-hexane and acetone were purchased from Merck, Germany. 4,4'-Methylenebis-(2,6-diisopropylaniline) (MBDIPA) and 4,4'-Methylenebis-(2-isopropyl-6-methylaniline) (MBIPMA) were purchased from Acros, Belgium. Fig. 3 shows the chemical structures of these compounds. All chemicals were used as received. A sample of primary

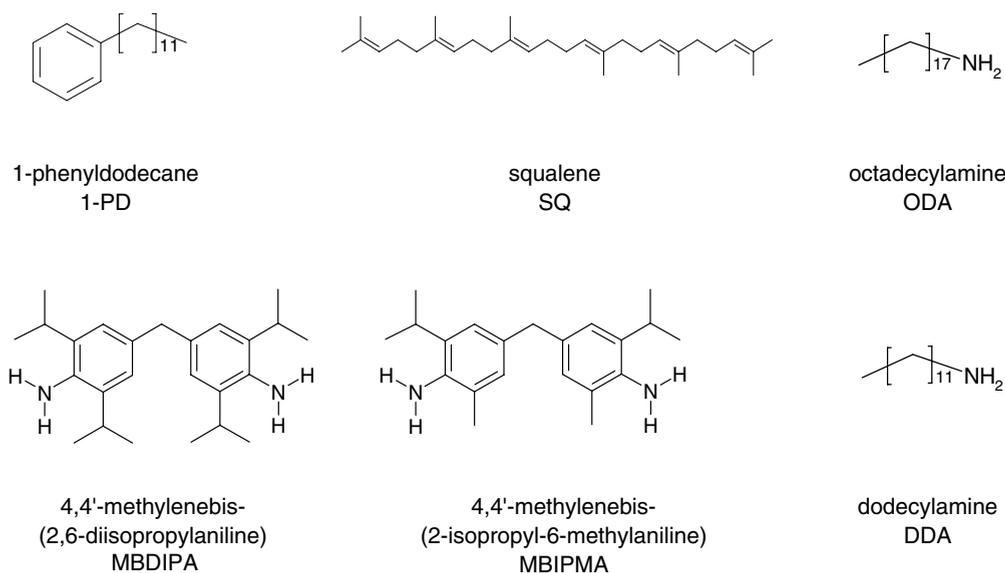


Fig. 3. Structures of selected extractants.

Table 1
Properties of different resins used in this research

Property	XAD-16	MPP	Stamypor
Material	pSty-DVB	Polypropylene	Polyethylene
Particle size (mm)	~0.5–0.71 ^a	0.8–1.18 (95%) 0.71–0.8 (2.5%) ^b	>1.18 (79%) 0.8–1.18 (19%) ^b
Maximum swelling with 1-PD or JM-T	~25–30 vol% ^c	Not observed	Not observed
Porosity	0.6 ^a	0.55 ^d	0.65 ^d
Pore size (nm)	20–30 ^a	500–1000 ^e	n.a.
Surface area (m ² /g)	764.62 ^f	11.51 ^f	7.17 ^f

^a Data obtained from the manufacturer.

^b Data obtained by sieving the particles.

^c Calculation based on the increase of the particle size (measured by sieving) of 8–10% after impregnation.

^d Estimation according to the amount of Primene[®] JM-T retained in the pores.

^e Estimation from the SEM image.

^f Data obtained by BET measurement.

amine Primene[®] JM-T was received from Rohm and Haas, Europe. Amberlite XAD-16 was purchased from Sigma Aldrich. Macroporous polypropylene (MPP) particles were donated by Akzo Nobel, the Netherlands. Macroporous polyethylene (Stamypor) particles were donated by Sabic, the Netherlands. The properties of particles used in this research are listed in Table 1.

2.2. Liquid–liquid equilibria

Liquid–liquid equilibrium experiments were conducted on a fully automated workstation, described by Kuzmanović et al. [17]. The extraction was done in closed 2-ml glass vials that were agitated for 24 h at 25 °C to ensure equilibrium. After agitation, the vials were transferred into thermostated (25 °C) trays, and a settling time of at least 2 h was allowed and shown to be sufficient. After settling, 70 µl samples of the aqueous phase were taken and diluted with 255 µl of ethanol to prevent phase separation and the evaporation of benzaldehyde. Finally, 25 µl of an internal standard solution (dibenzofuran in ethanol, 0.025 M for high concentrations and 0.0025 M for low concentrations of benzaldehyde) was added to the vial and quantitative analysis was done using a gas chromatograph, Varian CP-3800 system equipped with a capillary VF-5ms column (30 m, 0.25 mm; 0.50 µm packing) and a FID detector. Samples of known concentration of benzaldehyde were used for calibration. Accuracy of the analytical method was determined to hold within 2.5%.

The distribution ratio of benzaldehyde was calculated as the ratio of its concentration in the organic phase over its concentration in the aqueous phase.

The concentration of benzaldehyde in the organic phase was calculated from the mass balance.

2.3. Impregnation procedure

The impregnation procedure is based on the procedure published by Juang et al. [7]. Amberlite XAD-16 was first cleaned with acetone and *n*-hexane and then dried under vacuum at 60 °C, while MPP and Stamypor were cleaned only with acetone. Dry resin was then contacted with a mixture of *n*-hexane and amine or 1-PD. Dilution of amine and 1-PD in *n*-hexane was done only to assure a homogeneous loading of the particles. After a contact time of at least 3 h [9], *n*-hexane was removed by drying under vacuum at 60 °C. The loading of the resin with extractant was determined by measuring the increase of the mass. EIRs were also characterised by density, measured with helium pycnometer (AccuPyc 1330, Micromeritics).

2.4. Sorption equilibria

Batch adsorption experiments were used to determine the capacity of the EIRs. In each experiment, equal volumes of EIR (0.5 ml; determined by measuring mass and density) and equal volumes of 0.03 M aqueous solution of benzaldehyde (15 ml) were placed in a 50 ml glass-stoppered flask and shaken at 200 rpm and appropriate temperature for at least 24 h using the thermostated shaking bath (Julabo Shake Temp SW23), which was determined to be sufficient to reach equilibrium. All the volumes were determined by measuring mass and density. Finally, a 2-ml sample of the aqueous phase was removed

using a 2-ml syringe fitted with a filter (Schleicher & Schuel, Spartan 30/0,45 RC), and transferred to a 2-ml amber vial. Preparation and analysis of the samples were in parallel with the liquid–liquid experiments. The amount of benzaldehyde in the EIR particles was calculated from the mass balance.

2.5. Bleeding experiments

For determination of Primene[®] JM-T solubility in water, two phases were contacted, the equilibrium was reached and phase settling was allowed. Sample of the aqueous phase was taken with a syringe fitted with a filter (Schleicher & Schuel, Spartan 30/0,45 RC). To determine loss of the extractant from impregnated particles due to the solubility in water, similar experiments as for sorption equilibria were performed. EIRs were contacted with the same amount of water (instead of aqueous solution of benzaldehyde). The presence and concentration of Primene[®] JM-T in the aqueous phase was determined using a gas chromatograph, Varian CP-3800 system equipped with a capillary VF-5ms column (30 m, 0.25 mm; 0.50 μ m packing) and a FID detector. Prior to analysis, samples were preconcentrated in *n*-heptane. Calibration was done using the solutions of Primene[®] JM-T in *n*-heptane of a known concentration. As an internal standard, 0.0036 M solution of 1-phenyloctane in *n*-heptane was used. Since Primene[®] JM-T is a mixture of amines, it appears on a chromatogram as a cloud of peaks and therefore, for the quantification, a forced peak had to be introduced. Standard deviation of such analytical method was determined to be lower than 10%, which was accepted for the purpose of this research.

2.6. Kinetics experiments

Kinetics was investigated in a stirred vessel. 50 cm³ of aqueous solution of benzaldehyde was placed in the vessel. Initial concentration of the solution was 0.03 M. At time zero, 0.816 cm³ of impregnated resin was introduced to the reaction vessel. A 150 μ l of the solution phase was collected at various time intervals. Total number of samples was chosen to satisfy the criteria that total volume can be considered constant (difference in volume is less than 2.5%). Initial experiments were done to determine the optimal stirring speed, regarding the problem of mechanical damage of the particles or extractant loss. Additionally, if the intraparticle diffusion coefficients need to be estimated it is necessary that the

liquid film resistance is negligible. As a result, the optimal stirring speed was found to be 600 rpm, which was in agreement with the literature data [9].

3. Results and discussion

3.1. Extractant screening

Different amines were tested in order to find the most suitable extractant for further use in EIR technology. Selection was not only based on amine affinity for benzaldehyde recovery, but also on certain physical properties that can assure its successful application in EIR technology. The most important features were (non) solubility in water and fluidity at room conditions. Most of the amines with a large organic tail are, however, solid at room conditions. Therefore, it was necessary to dissolve them in a solvent. The solvent should be insoluble in water, but able to dissolve these amines. Fig. 4 shows the results of the extractant screening experiments for

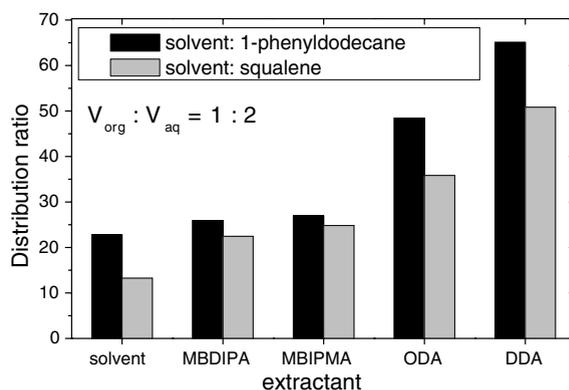


Fig. 4. Distribution ratio of benzaldehyde for different solvent and extractant combinations.

Table 2
Concentrations of saturated solutions of different amines in organic solvents

Amine	Solvent	Saturation concentration mol/l
MBDIPA	1-Phenyldodecane	0.368
	Squalene	0.489
MBIPMA	1-Phenyldodecane	0.181
	Squalene	0.211
ODA	1-Phenyldodecane	0.024
	Squalene	0.022
DDA	1-Phenyldodecane	0.068
	Squalene	0.040

benzaldehyde. An aqueous solution of benzaldehyde was contacted with nearly saturated solutions of amines in organic solvent. The corresponding concentrations are listed in Table 2. For comparison, the distribution ratio is defined as the ratio of benzaldehyde concentration in organic phase over its concentration in the aqueous phase in equilibrium.

The first two selected extractants, MBDIPA and MBIPMA, are aromatic amines with two amino groups. As shown in Fig. 4, they do not give a significant increase in distribution ratio compared to the pure solvent. The aromatic ring stabilizes the amino groups through the delocalization of the unshared electron pair of nitrogen over the ortho and para positions of the ring [15]. Additionally, there might be some steric hindrances as well. Consecutively, it becomes much less reactive. On the other hand, aliphatic amines (ODA, DDA) show a significant increase in distribution ratio towards benzaldehyde, although their saturation concentrations are much lower than those of aromatic amines. The difference between DDA and ODA is due to the difference in concentration. Although trends are the same, squalene shows lower capacities in all cases.

It can be concluded that for this application the extractant should be an aliphatic amine, insoluble in water, and, for a feasible process, should be present in high concentrations. Primene[®] JM-T fulfils these criteria. It is a mixture of isomeric primary aliphatic amines in the C18–22 range, with a highly branched alkyl chain in which the amino nitrogen atom is linked to a tertiary carbon. It is not a very viscous liquid (viscosity is reported to be $13.9 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ at 22.8 °C [18]) and therefore it does not require an additional solvent. In Fig. 5, dis-

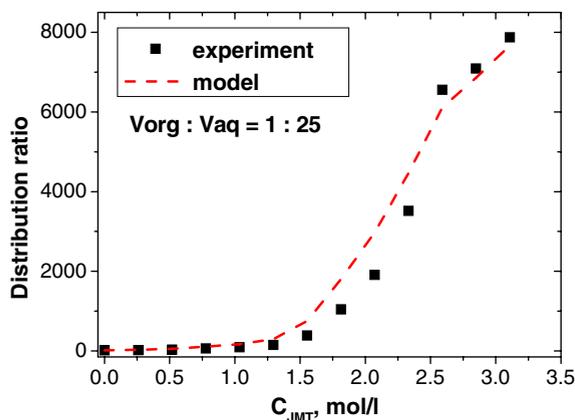


Fig. 5. Distribution ratio of benzaldehyde as a function of Primene[®] JM-T concentration in *n*-hexane at 25 °C.

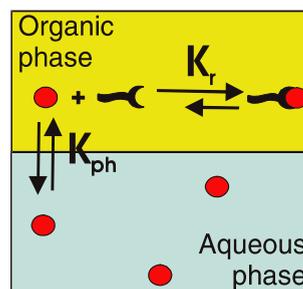


Fig. 6. Schematic representation of the reactive liquid–liquid equilibria.

tribution ratios are presented as a function of Primene[®] JM-T concentration in *n*-hexane. The last point represents distribution ratio obtained with pure amine. Results show an increase of the distribution ratio with the increase of the amine concentration. This proves the necessity to use high amine concentrations or if possible pure amine. The obtained experimental data can be satisfactorily described with a simple equilibrium model presented with Eqs. (1)–(6) and Fig. 6. Since the scope of this work was the exploration of the applicability of EIR technique rather than detailed (extensive) thermodynamic modelling, the equilibrium was described with as few parameters as possible. Therefore, it was assumed that activity coefficients are equal to 1 and activities could be replaced with concentrations.

The reaction equilibrium constant is defined in Eq. (1). C represents the concentration in mol/l. Subscripts Ald and Am stand for aldehyde and amine, respectively, while AldAm stands for the complex formed by aldehyde and amine (Schiff base). Superscripts org and aq indicate organic and aqueous phase, respectively. It was assumed that the concentration of water is constant and therefore can be incorporated in the equilibrium constant

$$K_r = \frac{C_{\text{AldAm}}^{\text{org}}}{C_{\text{Ald}}^{\text{org}} \cdot C_{\text{Am}}^{\text{org}}} \quad (1)$$

The physical partitioning ratio of aldehyde is given in Eq. (2). It was assumed that it remains constant throughout the whole range of concentrations used in this work

$$K_{\text{ph}} = \frac{C_{\text{Ald}}^{\text{org}}}{C_{\text{Ald}}^{\text{aq}}} \quad (2)$$

The overall equilibrium, as a consequence of physical and reaction equilibria, is expressed with the overall distribution ratio of the aldehyde (Eq. (3))

$$D = \frac{C_{\text{Ald}}^{\text{org}} + C_{\text{AldAm}}^{\text{org}}}{C_{\text{Ald}}^{\text{aq}}} \quad (3)$$

To solve this model, mass balances for all the species present in the system are applied (Eqs. 4 and 5)

$$(C_{\text{Ald,o}}^{\text{aq}} - C_{\text{Ald}}^{\text{aq}}) \cdot V^{\text{aq}} = (C_{\text{Ald}}^{\text{org}} + C_{\text{AldAm}}^{\text{org}}) \cdot V^{\text{org}} \quad (4)$$

$$C_{\text{Am,o}}^{\text{org}} = C_{\text{Am}}^{\text{org}} + C_{\text{AldAm}}^{\text{org}} \quad (5)$$

By combining Eqs. (1)–(5) the overall distribution coefficient of aldehyde in the system is obtained as an implicit function of the system parameters (K_r , K_{ph} , V_{org} , V_{aq}) and the initial concentrations of amine in the organic phase and aldehyde in the aqueous phase (Eq. (6))

$$D = K_{\text{ph}} \cdot \left[1 + K_r \frac{C_{\text{Am,o}}^{\text{org}} \cdot \left(1 + \frac{V_{\text{org}}}{V_{\text{aq}}} D \right)}{1 + \frac{V_{\text{org}}}{V_{\text{aq}}} D + K_r \cdot K_{\text{ph}} \cdot C_{\text{Ald,o}}^{\text{aq}}} \right] \quad (6)$$

Eq. (6) was used to fit the experimental data by minimizing the sum of squares of the deviations between the fitting curve and experimental points. The unknown equilibrium constant K_r was used as the fitting parameter and an optimal value of $168 \pm 12 \text{ mol}^{-1}$ was obtained. Physical partitioning ratio of benzaldehyde between *n*-hexane and water, K_{ph} , was obtained from an independent experiment. The value obtained is 14.8 ± 1.5 .

3.2. EIR performance

The most promising extractant, Primene[®] JM-T, was immobilized. Resins impregnated with the amine were compared with non-impregnated resins and resins impregnated with a non-reactive solvent. The results are presented in Fig. 7 and the corresponding extractant loadings given in Table 3. For

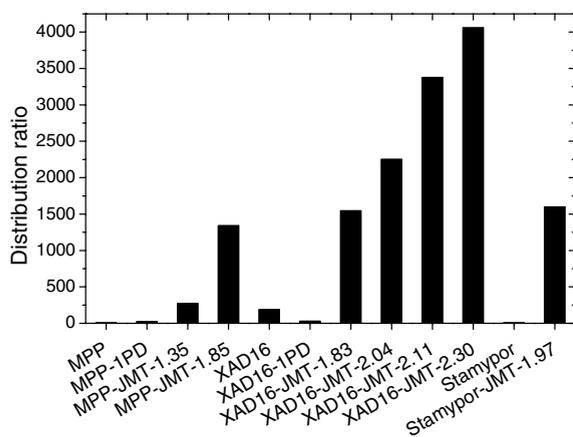


Fig. 7. Distribution ratios of different EIRs for removal of benzaldehyde at 25 °C.

Table 3
Loading of extractant

Resin	Extractant	Loading mol/l EIR
MPP	–	n.a.
	1-PD	2.02
	JM-T	1.35
	JM-T	1.85
XAD-16	–	n.a.
	1-PD	2.51
	JM-T	1.83
	JM-T	2.04
	JM-T	2.11
	JM-T	2.30
Stamypor	–	n.a.
	JM-T	1.97

comparison of different EIRs, the distribution ratio was defined as the ratio of benzaldehyde concentration in the EIR particle over its concentration in the aqueous phase (Eq. (7)). The concentration in the EIR phase was calculated according to the mass balance defined by Eq. (8). Equal volumes of EIR (0.5 ml) were compared. The EIR volume was defined as the total volume of particles

$$D = \frac{C_{\text{Ald}}^{\text{EIR}} + C_{\text{AldAm}}^{\text{EIR}}}{C_{\text{Ald}}^{\text{aq}}} \quad (7)$$

$$(C_{\text{Ald,o}}^{\text{aq}} - C_{\text{Ald}}^{\text{aq}}) \cdot V^{\text{aq}} = (C_{\text{Ald}}^{\text{EIR}} + C_{\text{AldAm}}^{\text{EIR}}) \cdot V^{\text{EIR}} \quad (8)$$

The affinity of unimpregnated MPP towards benzaldehyde is very poor. As can be seen from Fig. 7, by adding only a non-reactive solvent, in this case 1-phenyldodecane, the distribution ratio is increased seven times. If, instead, the reactive amine Primene[®] JM-T is added, then the capacity improvement is much higher. The distribution ratio can be increased up to 440 times compared to the unimpregnated MPP to a level of 1400 for a fully impregnated particle (3.71 molJMT/kgMPP, or 1.85 molJMT/l EIR).

Unimpregnated Stamypor exhibits the same behaviour towards benzaldehyde as MPP. Being more porous it can hold a higher amount of extractant. Therefore, distribution ratio for fully impregnated Stamypor is higher than the one of fully impregnated MPP.

Amberlite XAD-16 is a polystyrene-divinylbenzene particle, thus being aromatic it has some affinity towards aromatic compounds like benzaldehyde. Impregnation with a non-reactive solvent, such as 1-phenyldodecane, results in a decrease of its capacity. Possibly all the adsorption sites are blocked with 1-phenyldodecane and the solvent cannot compensate this loss. Simple physical solubility of benzaldehyde in 1-phenyldodecane is not sufficient enough.

On the other hand, if XAD-16 is impregnated with Primene® JM-T, its capacity is increased significantly up to a distribution ratio of 4000 for a fully loaded particle.

If the MPP and XAD-16 with similar loading of extractant are compared, it can be seen that the distribution ratios are almost equal. Actually, the distribution ratio of XAD-16 impregnated with Primene® JM-T is slightly higher than that of MPP. Probably XAD-16 is not fully impregnated and some active adsorption sites are left. Since they show affinity towards benzaldehyde, they can increase the capacity.

With the increase of the amine loading on the particle the distribution ratio is increased, which is shown for all tested polymeric supports. Therefore, it is desirable to have as much amine inside the particle as possible to increase the distribution ratio. Thus, better performance will be expected from a more porous particle.

3.3. Temperature influence

The reaction between primary amine and aldehyde is influenced by temperature, as shown by Kuzmanović et al. [19]. Therefore, it was expected that resins impregnated with Primene® JM-T could be regenerated by a temperature shift. Experiments were conducted at 25 °C, 50 °C and 75 °C and the corresponding isotherms are shown in Fig. 8. Sorption capacity q is defined as the amount of benzaldehyde retained per unit volume of EIR (Eq. (9))

$$q = \frac{n_{\text{Ald}}^{\text{EIR}} + n_{\text{AldAm}}^{\text{EIR}}}{V^{\text{EIR}}} \quad (9)$$

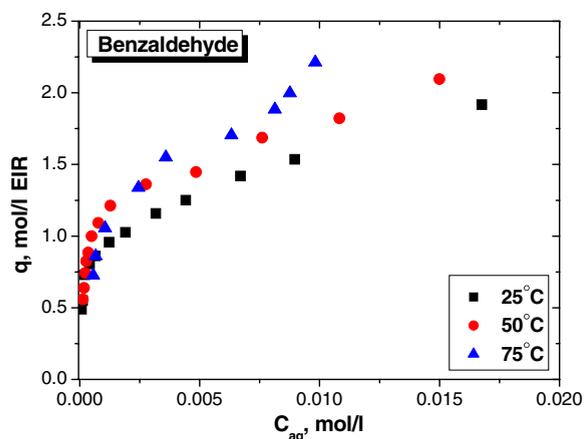


Fig. 8. Sorption capacities of fully impregnated MPP (1.85 mol JM-T/I EIR) for benzaldehyde at three different temperatures.

From the results in the low concentration region, it is clear that the reaction between benzaldehyde and Primene® JM-T is almost not influenced by temperature. In the higher benzaldehyde concentration region (higher than 0.005 mol/l), where the sorption is mainly influenced by the physical solubility, it can be seen that with temperature increase the sorption capacity is also increased. Possible explanation might be the fact that solubility of water in amine decreases significantly with the increase of temperature [20] and consequently shifts the equilibrium towards imine formation as illustrated by Fig. 2. Besides, the solubility of benzaldehyde in water decreases as well with the increase of temperature [21], and overall contributes to the mentioned effect.

3.4. EIR bleeding

The large hydrocarbon tail of Primene® JM-T consisting of 18–22 carbon atoms ensures a very low solubility in water. Determination of the exact value of Primene® JM-T solubility in water proved to be difficult because preliminary experiments showed very rapidly declining concentrations, which was most probably caused by the microemulsion or high affinity of amine for glass wall. The same effect was observed by Dave and Lidman [22]. Nevertheless, in our experiment, after allowing phase separation for few days, solubility was measured to be in the range of 4–5 ppm. This value corresponds to the solubility of other comparable aliphatic amines [20,22,23].

After immobilization of Primene® JM-T in MPP and XAD-16 particles, its solubility in water even decreases further due to the physical sorption. With the analytical method used, it was not possible to determine the exact value due to the very low concentration of the immobilized Primene® JM-T in water, but it is obvious from the chromatogram (Fig. 9) that amine peak completely disappeared, indicating that the concentration will be considerably below 1 ppm. These values should be treated with caution due to the very low concentrations which are in the lower limit of detection of the applied analytical technique. Nevertheless, a similar effect of the decrease of solubility in water after immobilization was also reported in the work of Traving et al. [9] for tri-*n*-octylamine immobilized on XAD-4 and XAD-16 particles.

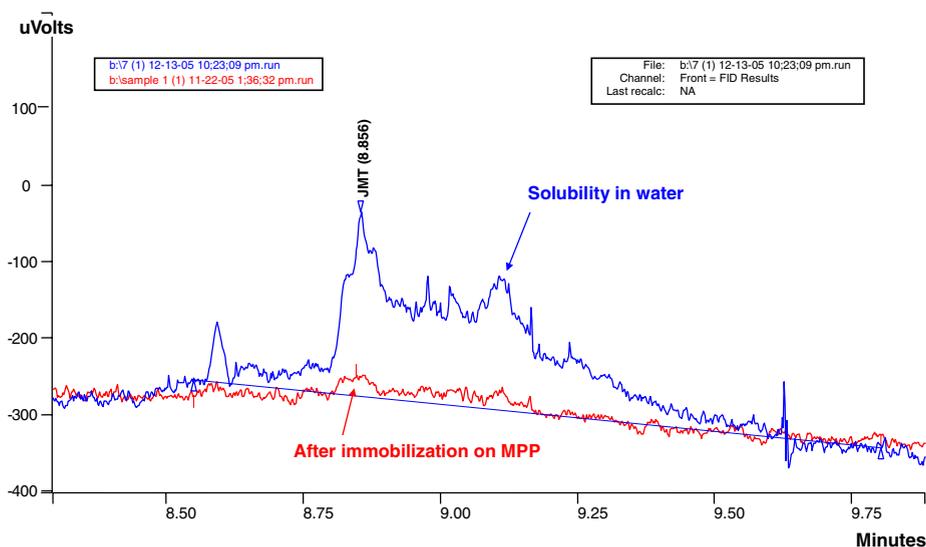


Fig. 9. Detail of a typical chromatogram of the Primene[®] JM-T on CP-Sil 5 column: blue – solubility of Primene[®] JM-T in water (4–5 ppm), red – after immobilization on MPP (lower than 1 ppm). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.5. Kinetics

The evolution of the benzaldehyde concentration in the aqueous phase with time is shown in Fig. 10 for both MPP and XAD-16 resins fully impregnated with Primene[®] JM-T. Impregnated Stamypor particles were also investigated but they showed very poor mechanical strength, and therefore were not suitable for this examination. It can be seen that MPP and XAD-16 have similar equilibration times despite the fact that MPP is a much bigger particle. The explanation for that phenomenon might lie in the particle morphology (pore sizes). MPP has

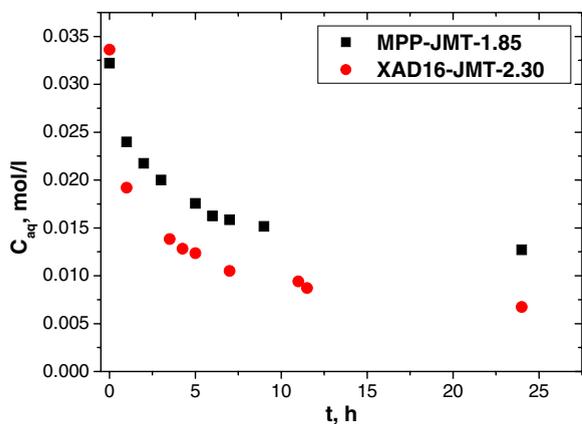


Fig. 10. Benzaldehyde concentration in aqueous phase as a function of time.

much larger pores with a narrow pore size distribution and a very low percentage of micropores caused by its partial crystalline structure. In comparison, XAD-16 has the amorphous structure and higher percentage of micropores.

The experimental results also show that sorption of benzaldehyde in these EIRs is rather slow. Since that might be a drawback for practical application of this technology, it is of a great importance to determine the rate controlling step. The overall extraction kinetics can be controlled by several mechanisms: (i) the diffusion through the liquid film surrounding the particle (film diffusion), (ii) intra-particle diffusion and (iii) chemical reaction; or combination of two or more of limiting steps.

At present, ion exchange kinetics is usually described by models such as the homogeneous particle diffusion model (HPDM) or the shrinking core model (SCM) [24]. The conventional shrinking core model assumes irreversible reaction which is not the case here. Therefore, it does not give a satisfactory description of the process.

The modified shrinking core model, derived by Bhandari et al. [25], developed for ion exchange, takes the reversibility of the process into account. This model was extended and applied to extractant impregnated resin kinetics by Juang et al. [26] to describe sorption of metal ions onto D2EHPA impregnated Amberlite XAD resins. Later it was successfully used by Escudero et al. [27] to describe

sorption of α -phenylglycine on trialkylmethylammonium chloride impregnated XAD-4. In all these applications, surface reaction between solute and impregnation liquid is assumed. In the system studied in this research, there is significant contribution of physical solubility of the solute in the extractant. However, in this study we adopted this model for preliminary determination of the rate controlling step. Since it is more thoroughly described elsewhere [25–27], here only the application to this system will be discussed. The fractional conversion of the EIR at time t is defined as

$$X = \frac{q(t)}{q_{\text{JMT}}} \quad (10)$$

where $q(t)$ (mol/l EIR) is the loading of the particle with benzaldehyde (in all its forms) at the specified time t and q_{JMT} is loading of the particle with the extractant. It is calculated from the experimental results. Fractional conversion of the outer surface of the EIR is given by

$$X_e = \frac{C_{\text{Ald}}^{\text{aq}}(t) \cdot K}{q_{\text{JMT}}} \quad (11)$$

where K is the equilibrium distribution ratio of benzaldehyde between particle and water

$$K = \frac{q}{C_{\text{Ald}}^{\text{aq}}} \quad (12)$$

It should be noted that every point on the EIR outer surface is in equilibrium with the solution outside the particle, so that both X and X_e are functions of time. According to the modified shrinking core model, the fractional conversion of EIR at any time is given by the following equations:

(a) For the film diffusion controlled process:

$$X = \frac{3D_f}{a \cdot \delta \cdot q_{\text{JMT}}} \int_0^t C_{\text{Ald}}^{\text{aq}}(t) dt \quad (13)$$

(b) For the particle diffusion controlled process:

$$Y = \frac{X_e}{K} \left[1 - 3 \cdot \left(1 - \frac{X}{X_e} \right)^{2/3} + 2 \cdot \left(1 - \frac{X}{X_e} \right) \right] \\ = \frac{6D_e b}{a^2 q} \int_0^t C_{\text{Ald}}^{\text{aq}}(t) dt \quad (14)$$

(c) For chemical reaction control:

$$Z = \frac{1}{K} \left[1 - \left(1 - \frac{X}{X_e} \right)^{1/3} \right] = \frac{K_c b}{a} \int_0^t C_{\text{Ald}}^{\text{aq}}(t) dt \quad (15)$$

where a is the average radius of the particle, δ is the thickness of the stagnant liquid film, b is the number of amine molecules reacted for each molecule of aldehyde (i.e. stoichiometric coefficient), D_e is the effective diffusivity in the resin phase, D_f is the diffusivity in the liquid film and K_c is the apparent chemical reaction rate constant.

According to the modified shrinking core model, the plot of X , Y , Z versus $\int_0^t C_{\text{Ald}}^{\text{aq}}(t) dt$ should give a straight line if the sorption process is controlled by that mechanism. $\int_0^t C_{\text{Ald}}^{\text{aq}}(t) dt$ was calculated from the experimental data using trapezoidal integration rule.

From Fig. 11, it is clear that no simple rate controlling step can be identified in the case of sorption of benzaldehyde on Primene[®] JM-T impregnated

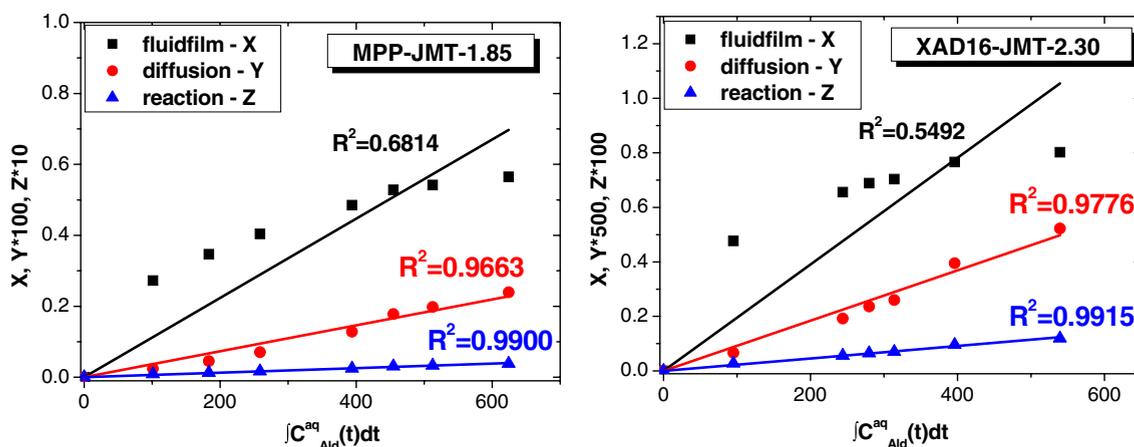


Fig. 11. Determination of the rate controlling step in the sorption of benzaldehyde with Primene[®] JM-T impregnated EIRs using modified shrinking core model.

particles. Most likely this sorption is controlled by both chemical reaction and particle diffusion. Since, however, no clear conclusion can be made, more rigorous modelling is needed as well as more experiments that can provide better insight in to the kinetics of this process. Nevertheless, it can be stated that the film diffusion resistance is not the rate controlling step confirming the validity of the performed experiments.

4. Conclusions

Branched aliphatic amines are high capacity extractants for aldehydes and being liquid at room conditions are suitable for application in EIR technology. Immobilized in macroporous particles, they still keep their favourable complexation properties resulting in very high distribution ratios.

The addition of an extractant can significantly increase adsorption capacity of otherwise very poor adsorbents, which is shown for the case of MPP and Stamytor particles. Particles with a higher porosity (Amberlite XAD-16) have the ability to immobilize a higher amount of extractant, which leads to a higher capacity.

Temperature has no significant influence on chemical reaction. On the other hand, it significantly influences physical equilibria. Solubility of water in amine significantly decreases with increasing temperature, as well as solubility of benzaldehyde in water. Overall, that leads to a higher capacity of EIR particles at higher temperatures and in higher aldehyde concentration range.

The stability of EIRs regarding the loss of the extractant due to the leakage in water was also studied. It was shown that immobilization reduces the extractant's solubility in water.

Kinetics of the sorption of benzaldehyde in EIRs impregnated with Primene® JM-T is rather slow. Simple analysis of experimental data using modified shrinking core model developed by Bhandari et al. showed that no clear rate controlling step can be pointed out and it is more likely that this sorption is controlled by both chemical reaction and diffusion in the particle. Therefore, more rigorous modelling is needed for accurate description of the kinetics.

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