

Effect of support properties on preparation process and adsorption performances of solvent impregnated resins



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ABSTRACT

The effect of support properties on preparation process and adsorption performances of solvent impregnated resins (SIRs) has been studied. Five SIRs were prepared by impregnating di(2-ethylhexyl)phosphoric acid (D2EHPA) in five macroporous adsorbent resins (MARs), respectively and used to extract V(IV) from aqueous solutions. The impregnation equilibrium can be fast achieved for the MARs with smaller pore size and bigger specific surface area, where D2EHPA is preferentially adsorbed in the micropores approximately as wall-spreading to form monolayer films, resulting in the relatively high utilization efficiency of extractant and stability of the SIRs. However, the extractant is more likely to accumulate in the macropores and/or mesopores than in the micropores, which leads to the higher mass ratio of extractant and pore-filling percentage in the SIRs with abundant macropores and/or mesopores. D2EHPA can be adsorbed on XAD-7HP fabricated with poly(methyl methacrylate) by virtue of relatively strong Hydrogen-bond, thus it can exist not only inside the pores but also on the surface of the resin, which causes the high mass ratio of extractant and extremely high pore-filling percentage although it contains the minimum pore volume. The relatively strong hydrogen-bond between XAD-7HP and D2EHPA is also believed to be responsible for its high adsorption capacity for V(IV) and utilization efficiency of the impregnated extractant.

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1. Introduction

In the 1970s, Warshawsky [1], Grinstead [2], Kroebel and Meyer [3] et al. put forward the conception of impregnated resins or solvent impregnated resins (SIRs) as a novel separation and recovery method. SIRs can be regarded as a liquid complexing agent dispersed homogeneously in a solid polymeric medium [4]. Herein the liquid complexing agent and solid polymeric medium are commonly known as the extractant dissolved in organic solvent and the support resins, respectively. SIRs have the merit of easy preparation by impregnating organic extractant into the support resins [5], which provides them with the advantages of solvent extraction (SX) and ion exchange (IX), such as high selectivity, lack of solvent emulsification, fast mass-transfer rate, operational simplicity and so on [6,7].

The extractant in SIRs should behave as a liquid state and also exhibit strong affinity to the matrix of support resins [8]. Commonly, the macroporous adsorbent resins (MARs) with high specific surface area (S_{BET}), abundant pores and stable chemical and/or physical properties which are in favor of adsorbing the extractant are considered as applicable supports for the preparation of SIRs [9]. It is generally acknowledged

that physical adsorption or π - π interaction is the dominant way for the adhesion of extractant into the pores of MARs [5,10]. The adhesion strength may be significantly varied as a consequence of the support properties such as pore structure, S_{BET} , matrix and so forth, which leads to different preparation process and adsorption performances of SIRs. Thus, it is convinced that the preparation and adsorption characteristics of SIRs are closely related to the support properties. However, most studies about SIRs have paid close attention to their application in the separation and recovery of metal ions [11–13] and organics [14, 15] from aqueous solutions. Few literatures focused on this relation between the support properties and preparation process and adsorption performances of SIRs.

Jeřábek et al. [16] studied the relationship between polymer support morphology and the impregnation process of di-(2-ethylhexyl)dithiophosphoric acid (DEHTPA) in alcoholic solution. It was proved that DEHTPA fills the pore space gradually from the smallest pores up to those with a diameter of approximately 10 nm. Strikovsky et al. [17] reported a novel phenomenon that the adsorption capacities of support for the extractant depend on the strength of the interaction between the functional groups of support and extractant, which means that the functional groups of support and extractant are important for the affinity between them. Long et al. [18] investigated the adsorption of naphthalene in the macroporous and hypercrosslinked

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Nomenclature

Abbreviations

AFM	atomic force microscopy
BET	Brunauer-Emmett-Teller
C.P.	chemically pure
D	pore diameter
D2EHPA	di(2-ethylhexyl) phosphoric acid
DEHTPA	di-(2-ethylhexyl)dithiophosphoric acid
IL	ion liquid
IUPAC	International Union of Pure and Applied Chemistry
IX	ion exchange
MAR	macroporous adsorbent resin
NADI	N ₂ adsorption-desorption isotherm
PMMA	Poly(methyl methacrylate)
PS/DVB	Poly(styrene-divinylbenzene)
PSD	pore size distribution
S _{BET}	specific surface area
SIR	solvent impregnated resin
STP	Standard Temperature and Pressure
SX	solvent extraction
VS	vanadyl sulfate

Symbols

C ₀	initial concentration of V(IV), mg/L
C _e	equilibrium concentration of V(IV), mg/L
C _E	equilibrium concentration of D2EHPA, g/L
K _L	empirical parameter of Langmuir isotherm, L/g
m	weight of dry MARs, g
n	molarity, mmol/g
P	pressure, KPa
P ₀	standard pressure, 100 KPa
Q ₀	saturated adsorption capacity of MAR for D2EHPA, g/g
Q _E	mass ratio of D2EHPA loaded on SIRs, g/g
Q _F	pore-filling percentage, %
Q _M	adsorbing capacity of SIRs for V(IV), mg/g
V	volume, mL
W	weight of dry SIRs, g

Subscripts

avg	average
E	extractant (D2EHPA)
M	metal ion (V(IV))
mic	micropore
tol	total

polymeric adsorbent. It was concluded that the pore structure of the support should be a more important factor than S_{BET} for the naphthalene adsorption in two polymeric adsorbents (XAD-4 and NDA-150), and the adsorption rate of naphthalene in XAD-4 is faster than that in NDA-150 because the former has more suitable pore structure for the transfer of the adsorbate in the adsorption sites based on the kinetic data. In the studies of Bokhove et al. [19,20], a series of macroporous resins were impregnated with 4-nonylphenol and applied in removing 4-Cyanopyridine to investigate the effect of the resin properties on the capacity, selectivity and mass-transfer rates of the SIRs. They found that the capacity and selectivity rest with the solvent properties but the mass-transfer rates are primarily determined by particle size other than porosity. Recently, Lira et al. [21] investigated the impact of the textural characteristics of the support on Au(III) sorption from HCl solutions using Cyphos IL101-impregnated Amberlite resins. It was concluded that the styrene-divinylbenzene-based resins are not able to bind Au(III) in hydrochloric acid solutions, but the acrylic ester-based

resins can fix the metal to some extent, suggesting that the support is also important for metal adsorption in SIRs.

The current work aims to probe the effect of the support properties on preparation process and adsorption performances of SIRs and provide some interesting information on the selection of support for the preparation of SIRs. In terms of preparation process of SIRs, the impregnation equilibrium time and the amount of extractant in SIRs were investigated. In the case of adsorption performances, two main evaluation indicators, the utilization efficiency of extractant and the stability of SIRs, were proposed to assess them. Five kinds of MARs, which possess different pore structure, S_{BET}, matrix and so forth, were chosen as comparable supports for the preparation of SIRs. The adsorption performances of these SIRs were investigated by adsorbing V(IV) from aqueous solutions. Di(2-ethylhexyl)phosphoric acid (D2EHPA) was chosen as the extractant because it has already showed satisfying extraction ability for V(IV) [22–24] and widely used in the preparation of SIRs [25–27].

2. Experimental

2.1. Materials

Four MARs, Dowex™ Optipore™ L493 (L493), Amberlite® XAD-4 (XAD-4), Amberlite® XAD-7HP (XAD-7HP), and Amberlite® XAD-16HP (XAD-16HP), were supplied by Shanghai Anland Biological Science and Technology Co., Ltd., China. The other MAR, Zhengguang SD300 (SD300) was purchased from Zhejiang Zhengguang Industrial Co., Ltd., China. These MARs were immersed in ethanol for 4 h and washed with 5 wt% hydrochloric acid in order to remove remaining monomers and other types of impurities which may be produced in the fabrication process, followed by washing with deionized water, and then dried at 60 °C in a vacuum oven for 24 h before impregnation. D2EHPA with C.P. grade, whose molecular structure is shown in Fig. 1, was purchased from Sinopharm Chemical Reagent Co., Ltd., China. The properties of D2EHPA used are given in Table 1. Vanadyl sulfate (VOSO₄·xH₂O) with C.P. grade was ordered from Alfa Aesar (Tianjin) Chemical Co., Ltd., China for preparing V(IV) solutions.

2.2. Preparation of SIRs

In this study, the dry method was adopted for the preparation of SIRs because it is commonly used and easy to determine the mass ratio of extractant in SIRs [28]. Dry MARs (1.00 g) were immersed in 20 mL D2EHPA-ethanol mixture with 50 vol% of D2EHPA, which was shaken by a constant temperature bath oscillator for certain time at 298 K. Then the resins were separated by filtration using a Buchner funnel and washed with deionized water. The redundant organic solvent was

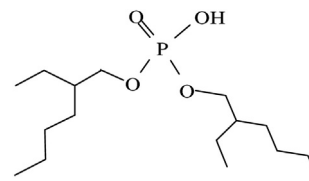


Fig. 1. Molecular structure of D2EHPA (C₁₆H₃₅O₄P).

Table 1
Properties of D2EHPA used.

Appearance	Colorless and transparent sticky liquid
Density	0.973 g/mL at 25 °C
Molecular weight	322.48 g/mol
Mass concentration	95%

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