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Successful recovery and concentration of vanillin and syringaldehyde onto a polymeric adsorbent with ethanol/water solution

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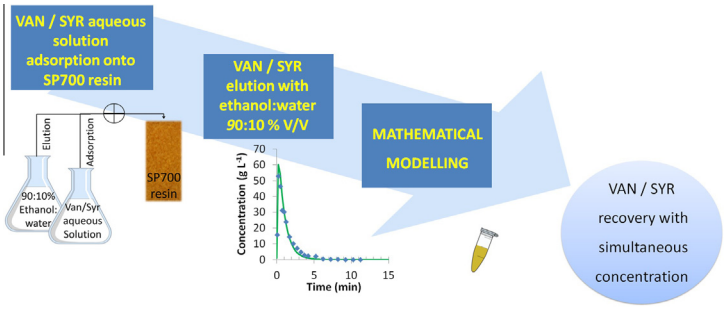
HIGHLIGHTS

- Vanillin/syringaldehyde (V/S) adsorption in ethanol:water (EW) onto SP700 was studied.
- Adsorbed amount of V/S is 68/83 times higher in water than in EW.
- After V/S adsorption from aqueous solution, more than 84% was desorbed with 6BV of EW.
- Concentration factors of 19- to 67-fold, depending on the loaded amount, were achieved.
- Modeling of the adsorption was performed with Linear and Freundlich isotherms.

GRAPHICAL ABSTRACT



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ABSTRACT

The recovery of purified fractions of vanillin and syringaldehyde (V&S) from an oxidized lignin medium has attracted considerable attention driven by the high added value of these products and the importance of lignin valorization processes in biorefineries. Polymeric resins with high specific area can be a viable option for the adsorption of aromatic compounds in polar solvents and desorption with less polar solvents for their recovery.

In this work, mono-component batch and fixed bed adsorption experiments were performed with V&S on Sepabeads SP700 in ethanol:water (90:10, % V/V) solutions to obtain the respective isotherm models at 298 K and 313 K. The adsorption behaviors of V&S were described by Linear and Freundlich models.

On the perspective of the real application of Sepabeads SP700 for recovery of V&S, fixed bed was first loaded with an aqueous solution of each compound and then desorption was performed with ethanol: water (90:10, % V/V). More than 84% of each compound was readily desorbed within 6 bed volumes, yielding concentration factors between 19-fold and 67-fold, relative to the inlet feed concentration.

The desorption histories at the outlet of the fixed bed were successfully described by the mathematical model comprising the equilibrium isotherms and linear driving force rate equations to describe the diffusional mass transfer inside the resin.

This work demonstrates that the adsorption of V&S from aqueous solution into Sepabeads SP700 bed and desorption with ethanol:water (90:10, % V/V) solution is a promising approach for the recovery of these compounds from lignin oxidation mixture. The high level of concentration achieved with this strategy and the type of solvent used is favorable for any further processing step, such as crystallization or spray drying.

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Nomenclature

$C_{i,e}$	equilibrium concentration of species '*i*' in the bulk solution ($g\ L^{-1}$)
$C_{i,0}$	initial concentration of species '*i*' (batch bottle point method) ($g\ L^{-1}$)
$C_{i,feed}$	concentration at column inlet for the species '*i*' ($g\ L^{-1}$)
C_i	concentration in the bulk fluid phase for the species '*i*' ($g\ L^{-1}$)
d_p	particle diameter (m)
D_{ax}	axial dispersion coefficient ($m^2\ min^{-1}$)
$D_{pe,i}$	effective pore diffusivity ($m^2\ min^{-1}$)
$D_{m,i}$	molecular diffusivity ($m^2\ min^{-1}$)
f_h	dry particle to wet particle mass ratio ($g_{dry\ resin}\ g^{-1}_{resin}$)
K_{Lin}	equilibrium distribution coefficient for Linear isotherm ($L\ g^{-1}_{dry\ resin}$)
K_F	Freundlich constant ($g\ g^{-1}_{dry\ resin}$) ($L\ g^{-1}$)$^{1/n}$
k_s	overall effective mass transfer coefficient (which includes intraparticle and film mass resistances) (min^{-1})
k_f	external film mass transfer coefficient ($m\ min^{-1}$)
k_{LDF}	linear driving force kinetic rate constant (min^{-1})
L_b	bed length (m)
n	Freundlich exponent (dimensionless)
Pe	Peclet number (dimensionless)
$q_{i,e}$	adsorbed phase concentration of species '*i*' at equilibrium ($g\ g^{-1}_{dry\ resin}$),
$q_{i,feed}$	adsorbed phase concentration of species '*i*' in equilibrium with $C_{i,feed}$ ($g\ g^{-1}_{dry\ resin}$)
$q_{ads,exp}$	experimental adsorbed phase concentration ($g\ g^{-1}_{dry\ resin}$)
$q_{ads,theor}$	theoretical adsorbed phase concentration ($g\ g^{-1}_{dry\ resin}$)
$q_{des,exp}$	experimental desorbed phase concentration ($g\ g^{-1}_{dry\ resin}$)
$\frac{dq_i}{dC_i}$	slope of the adsorption equilibrium isotherm
q_i	average adsorbed phase concentration of species '*i*' in the adsorbent particles ($g\ g^{-1}_{dry\ resin}$)
q_i^*	adsorbed phase concentration of species '*i*' in equilibrium with the bulk concentration at time t in the position z ($g\ g^{-1}_{dry\ resin}$)
Q	flowrate ($m^3\ min^{-1}$)
r_p	radius of the adsorbent particle (m)
Re	Reynolds number (dimensionless)
Sh	Sherwood number (dimensionless)
Sc	Schmidt number (dimensionless)
t	time (min)
T	absolute temperature (K)
$t_{st,exp}$	experimental stoichiometric time (min)
$t_{st,theor}$	theoretical stoichiometric time (min)
u_i	interstitial velocity ($m\ min^{-1}$)
W	weight of dry resin (batch bottle point method) ($g_{dry\ resin}$)
V	solution volume (batch bottle point method) (L)
V_b	bed volume (m^3)
$V_{m,i}$	molar volume of solute at its normal boiling point ($cm^3\ mol^{-1}$)
z	axial position (m)

Greek letters

ε_P	particle porosity ($L_{pores}\ L^{-1}_{particle}$)
ε_b	bed porosity
μ	viscosity of the solution (cP)
ρ_{app}	particle apparent density ($g_{wet\ resin}\ L^{-1}_{wet\ resin}$)
τ	tortuosity factor (dimensionless)
φ	association factor of the solvent (dimensionless)
Ω	linear driving force factor (dimensionless)

Abbreviations

LDF	linear driving force
S	Syringaldehyde
V	Vanillin

1. Introduction

Lignin-rich side streams resulting from processing lignocellulosic biomass are promising feedstocks to produce materials, fuels and chemicals [1,2]. Oxidative depolymerization of lignin is one of many existing processes [1] and yields several value-added functionalized phenolic compounds [3], such as vanillin and syringaldehyde [1,4]. These aldehydes are important ingredients for flavor and fragrance industry [5–7] and intermediates of fine chemicals such as 3,4,5-trimethoxybenzaldehyde [8] or levodopa [9].

The demand for obtaining purified fractions of vanillin and syringaldehyde using greener methodologies and lower environmental impact technologies led to an increase of adsorption studies already summarized elsewhere [10]. Additionally, adsorption processes are widely studied and referred to as a promising technology to recover phenolic compounds from numerous sources. An extensive review about the adsorption of phenolic compounds onto several types of adsorbents and practical cases was published by Soto et al. [11].

In the recent years, vanillin and syringaldehyde adsorption studies employing polymeric resins has increased [12–19] due to their enhanced capacities of adsorption, chemical stability and inertness and, most of all, due to the fact that recovery and regeneration of these compounds can be performed all together in one step [20,21].

Regarding the recovery of vanillin and syringaldehyde from this type of resins, a previous study [19] has shown that using water as eluting agent can be very time consuming with the additional disadvantage of noteworthy compounds dilution, generating a high volume and thus, hindering the development of a feasible industrial process. The use of organic solvents can provide a good alternative to overcome this drawback.

The adsorption and desorption behavior of phenolic compounds onto polymeric adsorbents are explained by the solubility parameter. This parameter, also known as the Hildebrand solubility parameter [22], is defined as the square root of the cohesive energy density; since the cohesive energy density is obtained from the heat of vaporization, this parameter is related with the van der Waals forces holding the molecules together. In general, the Hildebrand's model follows the generic rule 'like likes like'; thus, it is expected that two solvents are miscible and have the same dissolving capabilities or one solute is soluble in a solvent if their intermolecular van der Waals attractive forces, cohesive energy density, and solubility parameter values are similar [23]. Considering this, the aromatic nonpolar adsorbent will be greatly selective for aromatic adsorbates, particularly in polar solvents such as water, where the adsorbate has limiting solubility. On the other side, the best elution or regenerating solvent is that with lower solubility parameter. Therefore, acetone, methanol or ethanol can be a good choice of eluents, recovering the solute from the adsorbent with minimum volume consumption. Nonetheless, the solubility