Chemical Engineering Journal 288 (2016) 869–879

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Adsorption of vanillin and syringaldehyde onto a macroporous polymeric resin

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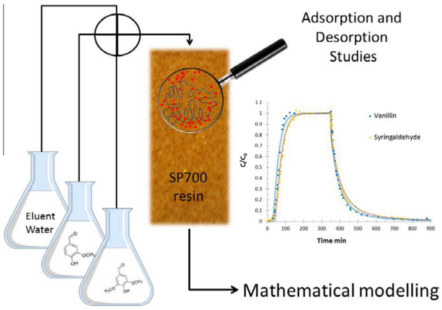
HIGHLIGHTS

- SP700 is a nonpolar resin suitable for vanillin (V) and syringaldehyde (S) adsorption.
- Batch experiments were successfully fitted with Langmuir and Freundlich models.
- Maximum adsorption capacities obtained: 0.663 (V) and 0.707 (S) $g\ g^{-1}{}_{dry\_resin}$.
- SP700 showed 46% more capacity for V than reported in literature for other resins.
- Fixed bed experiments were described with the axially dispersed plug flow model.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 October 2015
Received in revised form 11 December 2015
Accepted 12 December 2015
Available online 17 December 2015

Keywords:
Vanillin
Syringaldehyde
Adsorption
Nonpolar resin
Breakthrough

ABSTRACT

Pulp and paper mill and biorefinery side-streams are rich in lignin which can be partially converted to vanillin and syringaldehyde through an oxidation process. These value-added compounds can be recovered with an integrated separation process encompassing an adsorption step. In this work the potential of a macroporous polymeric resin, Sepabeads SP700, was assessed.

The resin was characterized regarding particle size, solid density, apparent density and particle porosity by means of laser dispersion, helium pycnometry and mercury intrusion porosimetry, respectively. Values within the ranges given by supplier were achieved: solid density, apparent density, particle size and particle porosity were 1294 $g\ L^{-1}$, 1012 $g\ L^{-1}$, 483 μm and 0.73 $mL_{pores}\ mL^{-1}_{particle}$, respectively.

Batch equilibrium isotherms for three different temperatures 283/288, 298 and 333 K were found for vanillin and syringaldehyde in aqueous solutions. Experimental results were fitted to Langmuir and Freundlich isotherm models. Equilibrium isotherms were validated by fixed bed studies at different temperatures and feed concentrations. A mathematical model comprising the equilibrium isotherms, linear driving force approximation, and intraparticle mass transfer resistances was used to describe the adsorption/desorption histories of concentration at the outlet of the fixed bed experiments. Although Langmuir model reasonably fit to the experimental results, the empirical Freundlich model was best to describe the experimental results for equilibrium concentrations bellow 1 $g\ L^{-1}$.

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http://dx.doi.org/10.1016/j.cej.2015.12.041
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Nomenclature

A	cross sectional area of the bed (m^2)
C_e	equilibrium concentration of the adsorbate in the bulk solution ($g\,L^{-1}$)
C_{feed}	initial feed concentration ($g\,L^{-1}$)
C_0	solute concentration at column inlet ($g\,L^{-1}$)
C	solute concentration at column outlet for time t ($g\,L^{-1}$)
C_i	concentration in the bulk fluid phase for the species i ($g\,L^{-1}$)
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 ($g_{dry\_resin}\,g^{-1}_{wet\_resin}$)
$\Delta H_{isosteric}$	isosteric adsorption enthalpy ($kJ\,mol^{-1}$)
K_L	constant related to the free energy of adsorption for Langmuir isotherm ($L\,g^{-1}$)
K_F	constant indicative of the relative capacity of the adsorbent for Freundlich isotherm ($(g\,g^{-1}_{dry\_resin})\,(L\,g^{-1})^{1/n}$)
k_{LDF}	linear driving force kinetic rate constant (min^{-1})
L_b	bed length (m)
Pe	Peclet number (dimensionless)
q_e	amount of solute adsorbed per dry weight unit of adsorbent at equilibrium ($g\,g^{-1}_{dry\_resin}$)
q_m	maximum adsorption capacity for Langmuir isotherm ($g\,g^{-1}_{dry\_resin}$)
q_0	amount of solute adsorbed in equilibrium with C_0 ($g\,g^{-1}_{dry\_resin}$)
q_{ads}	adsorbed amount ($g\,g^{-1}_{dry\_resin}$)
$q_{ads,exp}$	experimental adsorbed amount ($g\,g^{-1}_{dry\_resin}$)
$q_{ads,theor}$	theoretical adsorbed amount ($g\,g^{-1}_{dry\_resin}$)
q_{des}	desorbed amount ($g\,g^{-1}_{dry\_resin}$)
$\frac{dq_i^*}{dC_i}$	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 in equilibrium with the bulk concentration at time t and position z ($g\,g^{-1}_{dry\_resin}$)
Q	flow rate ($m^3\,min^{-1}$)
R	ideal gas constant ($kJ\,mol^{-1}\,K^{-1}$)
r_p	radius of the adsorbent particle (m)
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 ($m\,min^{-1}$)
V_p	volume of pores ($L_{pores}\,g^{-1}_{dry\_resin}$)
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_S	solid density ($g_{dry\_resin}\,L^{-1}_{dry\_resin}$)
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
pKa	acid dissociation constant

1. Introduction

Nowadays, industries worldwide are developing new strategies towards environmental and economic sustainable processes to provide efficient biomass conversion into bio-based chemicals, platform chemicals, fuels and energy [1].

Lignin is one of the most important components of side-streams from lignocellulosic-based biorefineries and pulp and paper industries and it has been considered for valorization due to its chemistry and properties. The oxidation of lignin at controlled conditions is one of the possible valorization routes, producing vanillin and syringaldehyde [2,3], among other compounds [4].

Vanillin and syringaldehyde are two phenolic aldehydes of great importance since they can be used as ingredients by flavor and fragrance industry [5–7] and as precursors of synthesis of several second-generation fine chemicals [8] such as 3,4,5-trimethoxybenzaldehyde, a building block of antibacterial agent trimethoprim [9] or levodopa, used for Parkinson's disease treatment [8]. Vanillin has the additional potential of being used as food preservative due to its antioxidant and antimicrobial properties [10,11]. Currently, 85% of vanillin world supply is synthesized from oil derived guaiacol and the remaining 15% come from lignin originated from softwoods [12], although an increase of vanillin produced from ferulic acid has also been reported [13]. Table S1 (Supplementary Material) summarizes the main physical and chemical properties of these aldehydes.

Several separation and purification sequences to obtain purified fractions of vanillin and syringaldehyde from oxidized lignin media, where a stage of solid–liquid adsorption is frequently included, have already been suggested and summarized elsewhere [14].

The majority of adsorption studies performed report the recovery of functionalized phenolic monomers from oxidized lignin medium by ion exchange resins being particularly focused on vanillin [15–17]. The application of zeolites has also been evaluated by Derouane and Powell [18].

To our knowledge adsorption studies conducted for mono-component aqueous solutions of syringaldehyde are inexistent. There is only one study in literature reporting the recovery of syringaldehyde from an oxygen delignification spent liquor with a polymeric resin [19].

Main studies with aqueous model vanillin solutions assessed the potential of ionic resins [20,21]. Recently, the application of polymeric resins to recover vanillin gained considerable interest [19,22–27] for many reasons: adsorption of phenolics onto nonpolar resins is feasible due to the existence of both hydrophobic and hydrophilic groups in the molecule; the pH is maintained constant along the process avoiding precipitation; these resins are chemically stable and inert being suitable for applications under a wide variety of conditions; phenolics recovery and resin regeneration can be performed simultaneously in one step; and their adsorptive properties can be modelled by the surface hydrophobicity, surface area and porosity [28]. The acid dissociation constant pKa of the adsorbate also determines the adsorption capacity [29]. The highest adsorption is achieved for the neutral form of the compounds, assured by a pH value of the solution higher than its pKa.

Phenolic compounds adsorption onto nonpolar resins is commonly explained by the occurrence of weak physical interactions mainly of the van der Waals forces type (e.g. permanent dipole-induced dipole or induced dipole-induced dipole) [29–31]. Since the phenolic compounds have hydrogen donors, some authors