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Adsorption behavior of levulinic acid onto microporous hyper-cross-linked polymers in aqueous solution: Equilibrium, thermodynamic, kinetic simulation and fixed-bed column studies

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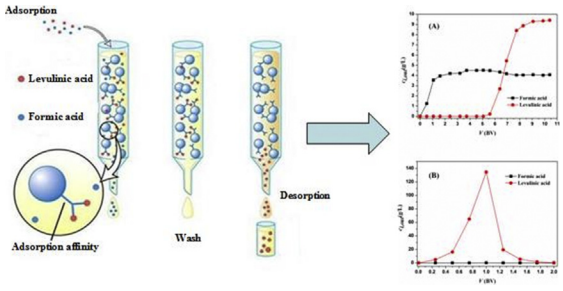
HIGHLIGHTS

- The feasibility of LA separation by a hyper-crossed-linked polymer was verified.
- The equilibrium, kinetic and thermodynamic properties of LA adsorption was studied.
- The process of LA from actual biomass hydrolysate was studied for the first time.
- The concentration of LA in the eluent was increased by 2.97 folds.

GRAPHICAL ABSTRACT



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ABSTRACT

The recovery of levulinic acid (LA) from aqueous solution and actual biomass hydrolysate by a microporous hyper-cross-linked polymer, SY-01, was investigated for the first time under batch and fixed-bed column conditions. The results showed that the optimum pH should be in the acidic range (pH < 3.0) without adjusting the pH. In the single-component system equilibrium study, the Langmuir isotherm model fits the LA adsorption onto SY-01 resin better than the Freundlich isotherm model, indicating that LA adsorption onto SY-01 resin under the concentration range studied is a monolayer homogeneous adsorption process. The maximum adsorption capacity of LA onto SY-01 resin decreased with increasing temperature, ranging from 103.74 to 95.70 mg/g. The obtained thermodynamic parameters suggested that the adsorption of LA on SY-01 was spontaneous (ΔG^0<−3.788 kJ/mol), and exothermic ($\Delta H^0 = -11.764$ kJ/mol). For kinetic study, the adsorption of LA onto SY-01 resin at various operating conditions follows the pore diffusion model and the intraparticle diffusion is the rate-limiting step for the adsorption of LA onto SY-01 resin. The effective pore diffusivity was dependent upon temperature, but independent of initial LA concentration, and were 3.306×10^{-10}, 5.274×10^{-10} and 7.707×10^{-10} m^2/s at 298, 318 and 338 K, respectively. In desorption process, the recovery efficiency of LA from SY-01 resin

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was 99.39%, and LA concentration in the eluent was raised 2.97-fold. In conclusion, our results show that the SY-01 resin has potential application in product recovery of LA from biomass hydrolysate.

1. Introduction

Nowadays, owing to world population increases and modernization, rising prices and decline of existing fossil resources and environmental pressures, the search for alternative biomass resources for the production of bio-based chemicals has received wide attention (Fang and Hanna, 2002; Ya'aini et al., 2013; Tang et al., 2014). In recent years, levulinic acid (LA) produced from abundant and relatively low cost lignocellulosic biomass has drawn considerable attention from researchers worldwide due to its potential as a platform for bio-based chemicals (Rackemann and Doherty, 2011). LA is a short chain fatty acid having a ketone carbonyl group and an acidic carboxyl group. These two functional groups make LA an ideal platform chemical for the synthesis of chemicals for applications including fuel additives, textile dye, animal feed, coating material, herbicides, pharmaceuticals and flavoring agents, solvents, plasticisers, anti-freeze agents, polymers, and resin precursors (Chang et al., 2007). The properties and potential industrial applications of LA and its derivatives have been reported in detail in several review papers (Rackemann and Doherty, 2011; Zhang et al., 2012).

To date, a substantial amount of patents and research articles have been reported for the manufacture of LA through acid-catalyzed dehydration and hydrolysis of hexose sugars (Fang and Hanna, 2002; Chang et al., 2007; Rackemann and Doherty, 2011; Zhang et al., 2012), while, on the other hand, only a limited number of investigations focused on the separation of LA from aqueous solution or biomass hydrolysate (Liu and Ren, 2006; Liu et al., 2009, 2010; Liu and Liu, 2011). Generally, the anion-exchange resin or activated carbon are frequently used for recovery of carboxylic acids from aqueous solution, fermentation broth or biomass hydrolysate (Nakano et al., 1996; Uslu, 2009; Uslu et al., 2010; da Silva and Miranda, 2013; Valentin et al., 2014). Liu et al (Liu and Ren, 2006; Liu et al., 2009, 2010; Liu and Liu, 2011) investigated the LA separation behavior on two weakly basic anion exchangers (D301 and D315) and column dynamics were also simulated using a model that considers external film mass transfer followed by intraparticle pore diffusion or parallel diffusion. Uslu et al. (Uslu et al., 2010) reported the removal of acetic acid and glycolic acid from aqueous solution using Amberlite IRA-67, a weakly basic gel-type polyacrylic resin with a tertiary amine functional group. The regeneration of resin was not studied in this literature. Alan Henrique da Silva and Everson Alves Miranda (da Silva and Miranda, 2013) reported adsorption/desorption of three various acids of different chain lengths (acetic, propionic and butyric acids) onto activated carbon and ion exchange resin. Nakano et al. (1996) reported high density culture of *Propionibacterium freudenreichii* couple with propionic acid removal system with activated charcoal. However, the pretreatment and desorption processes of ion exchange resin require acid and alkali (Liu and Ren, 2006; Qian et al., 2010), resulting in a large number of acid and alkali waste water, which increases the cost of separation. Activated carbon and other low cost adsorbents as well as nano adsorbents has been the most used adsorbent in removing organic contaminants from water or wastewater in industrial scale application owing to its large specific surface area and a predominant proportion of micropores (Ali and Gupta, 2006; Demirbas, 2008; Putra et al., 2009; Ali, 2010, 2012; Ali et al., 2011; Ali et al., 2012; Ali, 2014; Acosta et al., 2016). Nevertheless, it is limited due to its low selectivity, relatively expensive and difficult regeneration and reuse (Qu et al., 2013). To the author's knowledge, there is no published work on separating LA from aqueous solution or biomass hydrolysate using hyper-cross-linked adsorption resin. Therefore, seeking a suitable polymer resin adsorbent with high LA adsorption capacity, high adsorption selectivity, fast kinetics and high recovery of desorption is still a hot topic to researchers in the field of LA separation.

In our previous studies, a hyper-cross-linked polymeric adsorbent with proper microporosity and mesoporosity (SY-01 resin), was fabricated as a promising adsorbent for removal and recovery of inhibitor compounds from biobutanol fermentation wastewater (Lin et al., 2015). The SY-01 resin exhibited great potential for practical application due to its appropriate size for fixed-bed column packing, large adsorption uptake, easy regeneration and preference for butyric acid and color. This is mainly because of the butyric acid and color can be adsorbed onto SY-01 resin through π-π stacking formed between cross-linked benzene ring of resin and the alkyl chain of butyric acid, as well as hydrogen bonding between the amide groups and butyric acid, which played an important role in the adsorption. Hence, it is viable and economical for SY-01 resin to be used as the adsorbent material for separating LA from aqueous solution and actual biomass hydrolysate. We reported here, for the first time, that the SY-01 resin was attempted to use as an adsorbent to adsorb LA from aqueous solution and actual biomass hydrolysate under batch and fixed-bed column conditions.

This study focused on the feasibility of SY-01 resin to be applied as the adsorbent for adsorption system to recover LA from aqueous solution and actual biomass hydrolysate. In this study, the effects of the initial solution pH and the formic acid concentration on the adsorption of LA were investigated systematically and the optimum of pH value was selected. The experimental equilibrium isotherm data were fitted by the Langmuir and Freundlich isotherm models. The thermodynamics parameters including the free energy, enthalpy and entropy were calculated and discussed. The adsorption kinetics under various operating conditions were also investigated and predicted by pore diffusion model (PDM). In addition, the adsorption breakthrough/desorption curves for the dynamic adsorption/desorption of LA from actual biomass hydrolysate on fixed-bed column with SY-01 resin were carried out systematically.

2. Materials and methods

2.1. Materials

All the chemicals used were analytical reagent (AR) grade and purchased from Sinopharm Chemical Reagent Co., Ltd., China. The solution of LA with different concentrations was prepared by dissolving LA in deionized water. The SY-01 resin was provided by the Laboratory of Energy and Chemical Engineering, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences (Guangzhou, China). The detail characterization of the SY-01 resin in terms of scanning electron microscopy (SEM), nitrogen adsorption-desorption isotherms, Fourier transform infrared spectroscopy (FT-IR) and elemental analysis (EA) were given in our previous work (Lin et al., 2015).