Furfural removal from liquid effluents by adsorption onto commercial activated carbon in a batch heterogeneous reactor

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ARTICLE INFO

ABSTRACT

Currently, the presence of furfural at low concentrations in different industrial effluents presents an environmental problem. In this work, the optimization of the main operating conditions of a batch heterogeneous reactor for furfural removal by adsorption onto commercial activated carbon were determined. In this sense, the effect of the commercial activated carbon concentration, operating temperature, and the agitation rate in the reactor were studied. In all experiments, the adsorption data have engaged in behavior that can be represented by pseudo-second order model. In liquid effluents with initial concentrations of furfural equal to 1 or 2 g dm^{-3}, the 90% furfural removal requires a minimum concentration of adsorbent in the reactor equal to 11 or 12 g dm^{-3}, respectively. The optimum agitation rate and temperature were around 100 rpm and 303–308 K, respectively. Equilibrium data at different temperatures were represented by Langmuir equation. The thermodynamic parameters of activation energy ($E_a = 43.1$ kJ mol^{-1}) at different furfural concentrations, standard free energy ($\Delta G^\circ = -16.1$ kJ mol^{-1}), standard enthalpy ($\Delta H^\circ = -21.8$ kJ mol^{-1}), and standard entropy ($\Delta S^\circ = -18.8$ J mol^{-1} K^{-1}) of the adsorption process were determined.

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1. Introduction

Many industries such as petrochemical, pulp and paper, pharmaceutical, and food industries involve processes that use or produce furfural (Sahu et al., 2007). It is used as a chemical intermediate, weed killer, fungicide and as a flavoring agent (Othmer, 1984; Arts et al., 2004). Sulfite pulping process used in the pulp and paper industry is one of the sources of furfural contamination (Rivard and Grohmann, 1991).

Furfural is an organic compound that is stable in the room temperature and decomposes to CO and CO$_2$ at high temperature. Its solubility in water is about 83 g dm^{-3}. Furfural accidental ingestion can cause death and its absorption from skin will damage the neurotic system and the lungs of human beings (Othmer, 1984). Also, furfural is a heterocyclic aldehyde produced by dehydrating at high temperatures of xylose (Montané et al., 2002). Therefore, it is a characteristic compound present in acid hydrolyzates in which

the furfural concentration can usually reach 2–3 g dm^{-3}. At high concentrations (>1 g dm^{-3}), furfural inhibits growth and metabolic activity of yeasts cultures (Peng et al., 2007). These effects are important, since inhibition caused by furfural during respiratory growth has a great impact on cell propagation in ethanol plants based on lignocellulosic feedstocks.

Furfural toxicity has been extensively studied in relation to ethanol production. *Escherichia coli* strain K011 has a maximum tolerance of 3 g dm^{-3}. Similar tolerances, e.g., 3–4 g dm^{-3} have been observed by other enteric bacteria, including those engineered for ethanol production (Boopathy et al., 1993; Zaldivar et al., 1999). However, culture growth and ethanol production begin to be effected at greater concentrations than 1 g dm^{-3} (Zaldivar et al., 1999). *Saccharomyces cerevisiae* and xylose fermenting yeasts, *Candida shehatae* and *Pichia stipitis*, have been observed to be almost completely inhibited by furfural concentrations of 2–4 g dm^{-3} (Delgenes et al., 1996; Palmqvist et al., 1999). Possible mechanisms for furfural toxicity include chemical reactivity with cellular components, damage to the cellular membrane, and inhibition of metabolism (Zaldivar et al., 1999; Tobias et al., 2002). The toxicity of furfural appears to be a function of its hydrophobicity.

Palmqvist et al. (1999) and Palmqvist and Hahn-Hagerdal (2000) demonstrated a correlation between toxicity and hydrophobicity for a number of inhibitors found in lignocellulose hydrolyzates.

Due to the actual and future need for renewable energy sources, lignocellulosic biomasses are considered as promising materials by the production of liquid fuels and chemicals. Xylose is the main hemicellulosic sugar and the second most abundant sugar in nature after glucose. The bioconversion from xylose to ethanol or xylitol is of interest as the first product is a clean fuel that acts as gasoline for cars and the second one is a sweetener with uses in the food industry. The research on yeast conversion of xylose to ethanol or xylitol has been intensively studied during the last decades (Cuevas et al., 2009; Moya et al., 2008).

The chemical treatment with diluted or concentrated inorganic acid solutions is well-established method for the low-cost production of xylose from green biomass because it promotes the effective hydrolysis of hemicelluloses that result in high recovery of bio-polymer as monomers in the hydrolyzate (Liu et al., 2012; Mateo et al., 2013). However, acid hydrolysis of biomass also led to production of different compounds (carboxylic acids, phenolic compounds, furans. . .) which act as fermentation inhibitors (Palmqvist and Hahn-Hagerdal, 2000). This has made that different techniques have been applied to remove inhibitors from hydrolyzates: overliming (Mohagheghi et al., 2006), solvent extraction (Zhu et al., 2011), nanofiltration (Weng et al., 2010), bio-detoxification (Zhang et al., 2013), adsorption (Lee et al., 2011), etc.

On the other hand, the separation of furfural from aqueous solutions is a significant field of study for the sake of industrial safety and environmental protection because many industries involve processes that produce or use furfural, so that when furfural comes in contact with water streams in those plants the aldehyde becomes a significant toxic component in their wastewater (World Health Organization, 2000).

Adsorption technology has become well established (Asgher and Bhatti, 2012a,b; Bhatti et al., 2012; Bhatti and Safa, 2012; Sadaf et al., 2013; Sadaf and Bhatti, 2013) and powerful technique for water treatment; being activated carbons the most effectively used adsorbents due to their adequate porosity and chemical features. Batch experiments are usually done to measure the effectiveness of adsorption for removing specific adsorbates as well as to determine the maximum adsorption capacity (Asgher and Bhatti, 2012a,b; Noreen et al., 2013). However, few investigations have been carried out on the adsorption of furfural onto activated carbon especially at a reactor scale.

In this study, the optimization of the adsorption process at batch reactor laboratory scale was performed to assess the effectiveness of a commercial activated carbon in the elimination of furfural. The effect of operation conditions at the reactor, such as contact time, temperature, agitation rate, and initial furfural concentration were investigated. The equilibrium was described by Langmuir isotherm. Also, kinetic and thermodynamic parameters were obtained to better understand the adsorption mechanism. These data are useful in the practical applications of the adsorbent such as detoxification processes of hydrolyzates, in the treatment of industrial polluted waters, and in other uses.

2. Materials and methods

2.1. Chemicals

In this study all experiments were carried out using furfural and commercial activated carbon as adsorbent. Furfural (2-furaldehyde, 99% (w/w), CAS Number 98-01-1) was purchased from Sigma–Aldrich (Spain). Commercial activated carbon (CAS Number 7440-44-0) was acquired from Panreac Química S.A. (Spain) with the following characteristics: Granular activated carbon No. 1 (chemically pure, Code: 211238), particle size: 1.25–3.15 mm, calcinations residue at 873 K = 6% (w/w).

2.2. Adsorption system

All experiments were performed in batch stirred tank built in Pyrex glass (heterogeneous reactor, Fig. 1). The reactor geometry is cylindrical (internal and external diameter were 9.5 and 12 cm, respectively) with round bottom and its useful volume is $0.5\,\mathrm{dm}^{-3}$ (corresponds to a height in the reactor equal to 7.7 cm). The four inputs of the reactor cap have different functions:

1. The central input of the reactor cap has inside/outside diameter equal to 29/32 mm which allows to entry a Teflon (PTFE) stirrer shaft with anchor type ending. The characteristic dimensions of the stirring system are the following: shaft diameter 0.6 cm, total length 50.7 cm, blade width 7.7 cm, anchor maximum height 3.3 cm, anchor diameter 0.9 cm. The height between the stirrer shaft and the bottom of the reactor 1 cm. The shutdown system type used is QuickFit stirrers ST20/4.
2. The three remaining inputs of the reactor cap have an internal/external diameter equal to 14/23 mm, which used to install a mercury thermometer, a total reflux condenser and the last input for sampling. The total reflux condenser (Coil condenser, Dimroth type) was used to prevent evaporation losses and thus ensure the correct determination of the concentrations of furfural.

The agitation system used consist of overhead stirrer (Heidolph type RZR-2000 motor) that has a digital torque setting and speed display that can operate at different agitation rates.

Temperature control system to avoid fluctuations formed by a distilled water bath and heater head that allows control of the temperature inside the reactor.

2.3. Adsorption experiments

For the study of furfural adsorption onto commercial activated carbon as adsorbent, the commercial activated carbon and the furfural solutions were introduced to the reactor, and the temperature control system was switched on. Experiments were carried out in a batch heterogeneous reactor with work capacity equal to $500\,\mathrm{cm}^3$. The different furfural solutions were prepared from a 2-furaldehyde, 99% (w/w) Sigma–Aldrich (Spain).

In this work, different experimental series were realized. The first one was conducted to address the influence of the commercial activated carbon concentration on the adsorption process. With this purpose, the following concentrations 5, 7, 9, 11, and $13\,\mathrm{g\,dm}^{-3}$ of commercial activated carbon were prepared for two different furfural concentrations 1 and $2\,\mathrm{g\,dm}^{-3}$. In the second series, experiments at different agitation rates values (0, 67, 150, and 250 rpm) were conducted. From the third to the seventh series, adsorption experiments were conducted at different temperatures, 298, 303, 308, and 313 K, and different furfural concentrations (0.1, 0.25, 0.50, 0.75, and $1.0\,\mathrm{g\,dm}^{-3}$) used for each temperature.

In all experimental of the first series the common adsorption conditions were 1 and $2\,\mathrm{g\,dm}^{-3}$ of furfural, pH 6.0, agitation rate 250 rpm, and temperature 303 K. In the second series the common adsorption conditions were $1\,\mathrm{g\,dm}^{-3}$ of furfural, pH 6.0, commercial activated carbon concentration $9\,\mathrm{g\,dm}^{-3}$, and temperature 303 K. From the third to the seventh series, the common adsorption conditions were pH 6, commercial activated carbon concentration