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Adsorption of Water and Ethanol by Canola Meal in a Batch Liquid System

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ABSTRACT In this paper, adsorption of water and ethanol from liquid phase using canola meal based adsorbents was investigated. The research is important as there is an interest in using bioethanol as a sustainable energy source. The conversion of carbohydrates to bioethanol through fermentation generally leads to a broth that contains 5-12 wt% of ethanol mixed with water and some other organics. In the ethanol industry, the recovery of ethanol from the fermentation broth to fuel grade is energy intensive and costly. Adsorption using biosorbents attracts increasingly interest due to low costs and non-toxicity to the environment.

Canola meal is abundantly produced as a by-product in canola industry. The objective of this work is to determine the capability of canola meal based adsorbents for adsorption of water from liquid ethanol mixture. The effects of canola meal particle size, contact time, temperature and water/ethanol concentration on water as well as ethanol uptake were examined. Separation factor of water over ethanol was also determined. Water uptake is constantly higher than that of ethanol while both water and ethanol uptake were fast and completed over 90% of the equilibrium values within the first 30 min. The results demonstrated that canola meal based adsorbents are able to selectively adsorb water from ethanol mixture to concentrate ethanol. Freundlich equation provided reasonably fit to the pseudo-equilibrium water and ethanol adsorption data. The results provided

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pioneer information on developing cost biosorbents for purifying ethanol and reducing the production costs of fuel ethanol.

Keywords: Biosorption, water adsorption, ethanol dehydration, adsorption kinetics and equilibrium, separation factor.

INTRODUCTION Protection of the global environment and depletion of the conventional hydrocarbon fuel supplies have motivated researchers to develop alternative fuels. Ethanol based biofuels, which can be used as blending components with hydrocarbon-based fuels, have been considered more extensively during the last two decades. With a high octane number and low emissions of carbon monoxide, volatile organic compounds and particulates, bioethanol makes an excellent gasoline blending component (Kumar et al. 2010; Frolkova and Raeva 2010). Bioethanol is generally produced through the fermentation of carbohydrates. The product of fermentation is a mixture containing 5-12 wt% of ethanol in water and some organics (Sun et al. 2007). The presence of water in ethanol is undesirable when blending with hydrocarbons. Consequently, there is a great interest to obtain anhydrous ethanol in order to use it as a fuel (Frolkova and Raeva 2010). However, separation of ethanol from the large amount of water is energy intensive process (Jeong et al. 2009). In order for ethanol to be considered as a substitute fuel, the energy consumed in the ethanol production industry should be reduced (Kumar et al. 2010).

The current method used in the industrial ethanol dehydration consists of distillation of fermentation strength ethanol to obtain a 75–92 wt% ethanol-water product which is below the azeotrope (95.6 wt% ethanol), followed by water adsorption using molecular sieves to obtain fuel grade ethanol (Sun et al. 2007). However, the commercial 3-A molecular sieves which are used in ethanol dehydration have low water uptake of 0.25 g /g dry adsorbent (Simo et al. 2009; Carmo and Gubulin 2006). They also need high temperature in the range of 190 - 210 °C for regeneration (Fahmi et al. 1999). Therefore, there has been a great interest in developing cost effective technology for ethanol dehydration process. A variety of starchy and cellulosic materials was used as adsorbents to remove water from ethanol-water vapor mixtures (Baylak et al. 2012; Chang et al. 2006; Chang et al. 2004; Chang 2001; Hong et al. 1982; Ladisch and Dyck 1979). It has been reported that corn grits have been used in the ethanol dehydration industry, which shows that biosorbents have the potential to be commercialized (Beery and Ladisch 2001). However, the water uptake of corn grit is as low as 0.2 g/g dry adsorbent and use of this biomaterial as an adsorbent can place pressure on food consumption. Attempts have been made using other types of biomaterials such as barley straw and wheat straw (Sun et al. 2007) and saw dust (Benson and George 2005).

A potential biomaterial which can be used as an adsorbent for ethanol dehydration is canola meal. A large amount of canola meal is produced in the canola industries due to oil extraction and biodiesel production. The commercial price of canola meal is about \$0.24 /kg, much cheaper than that of molecular sieves (\$3 - 120 /kg). The immediate benefits of canola meal commercialization as an adsorbent in the ethanol dehydration industry include low ethanol production cost and enhancement of agricultural industry by selling their waste products. Furthermore, increase in the ethanol production rate will benefit the environment. Preliminary results of using canola meal based adsorbent to remove water from water-ethanol vapor mixture was reported recently by our research team (Baylak et al. 2012). However, no results have been reported to elucidate the capacity of such biomaterial for water and ethanol adsorption directly from the liquid phase which is the product of fermentation for bioethanol production.

The objective of this work is to determine the capability of canola meal based adsorbents for adsorption of water from liquid ethanol mixture. To that end, water and ethanol uptakes by canola meal were determined and used to optimize the conditions for selective water uptake in ethanol-water mixtures. The effects of particle size of canola meal, temperature, contact time, and adsorption isotherm were studied.

EXPERIMENTAL SECTION

Biosorbents The canola meal used as an adsorbent was obtained from Co-op Feeds Saskatoon, Saskatchewan Canada. Canola meal was sieved in five particle size groups of 0.15 - 0.25 mm, 0.25 - 0.43 mm, 0.43 - 1.18 mm, 1.18 - 3.35 mm, and > 3.35mm, respectively. The biosorbent particles were then oven dried at 105°C for 24 hrs.

Feed solutions Ethanol water solutions with different concentrations were prepared by mixing anhydrous ethanol (reagent grade, Commercial Alcohols Inc., Canada) and deionized water.

Adsorption Procedure Samples were prepared by mixing 4 g dry canola meal and 150 g water, ethanol or a mixture of water and ethanol in 250 ml Erlenmeyer flasks on an orbital shaker at 130 rpm for a certain amount of time. The shaking speed was chosen by providing sufficient mixing but eliminating biomass rupture because of shear force. To determine the water and ethanol uptake of canola meal in pure water or ethanol solution, the weight difference of wet and dry biosorbent was divided by the weight of the dry biosorbent; while, the following equation which is based on the mass balance of water and ethanol in the system was used to determine the water and ethanol uptake in ethanol-water mixture.

$$q_{\text{exp}} = (C_0W_0 - C_tW_t) / w \quad (1)$$

C_0 and C_t are the ethanol or water concentrations in liquid phase at the beginning and at time t , respectively, (wt %). W_0 and W_t are the initial weight of solution and that at time t (g). w and q_{exp} represent the dry net biosorbent weight (g) and experimental uptake (g/ g dry biosorbent), respectively.

Analyses Water and ethanol content were determined by a Karl Fisher coulometer (Mettler Toledo DL32) and a Chemical Analyzer (Analox GM8), respectively.

RESULTS AND DISCUSSION

Effect of Particle Size The effects of biosorbent particle size on the uptake of water and ethanol was done by varying the particle sizes of canola meal as follows: : 0.15 - 0.25 mm, 0.25 - 0.43 mm, 0.43 - 1.18 mm, and 1.18 - 3.35 mm. Each sample consisted of 4 g of canola meal and 150 g pure water or pure ethanol shaken at 130 rpm on the shaker for 30 min.

The results are shown in Figure 1. The data are experimental results and the error bars represent 95% confidence intervals. The experimental results demonstrated that both ethanol and water uptake were increased as the particle sizes were decreased. This is because the smaller the particle size of canola meal, the higher the surface area available for adsorption, the faster the adsorption.

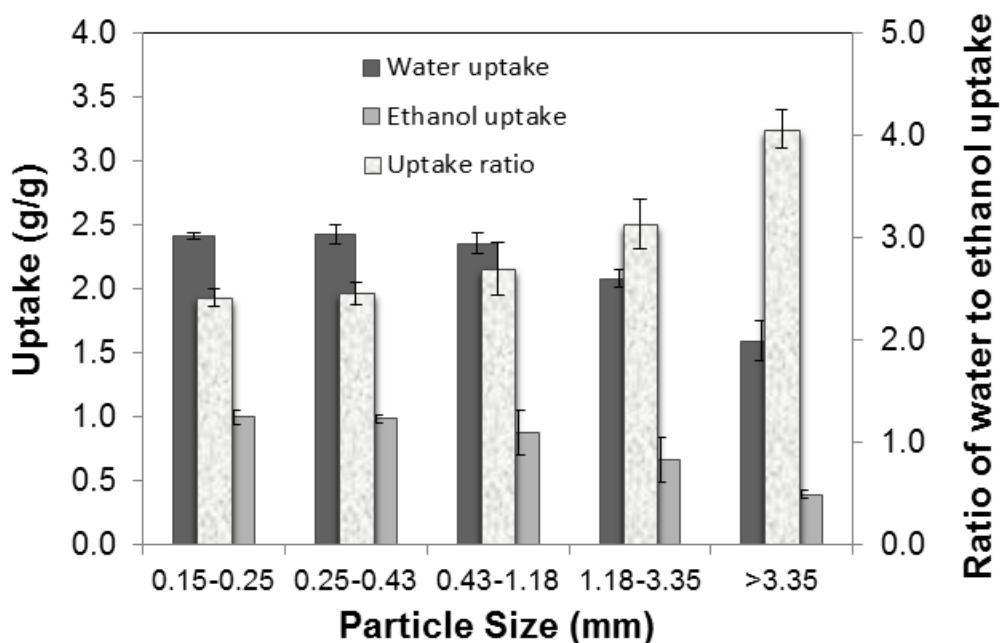


Figure 1. Effect of particle sizes of canola meal on water/ethanol uptake
 All experiments were run at 25 °C for 30 min. Each sample contained 4 g dry adsorbents and 150 g pure water or ethanol solution. Error bar stands for 95% confidence interval.

Optimum particle size does not only ensure high water uptake but also high ratio of water over ethanol uptake. Though water uptake increased at smaller particle sizes, the ratio of the water to ethanol uptake decreased, which is not desirable. For instance, water uptake is 2.08 g/g at the particle sizes of 1.18 – 3.35 mm, and ratio of water to ethanol uptake is 3.14. When the particle sizes were decreased to 0.43 - 1.18 mm, water uptake increased to 2.34 g/g but the ratio was decreased to 2.70. This is because ethanol uptake was increased as well at decreased particle sizes. The results are similar to water-ethanol uptake by cellulosic material barley straw (Sun et al. 2007). As a result, canola meal with particle sizes in the range of 1.18 - 3.35 mm were selected for the following investigation considering both higher water uptake and the ratio of water to ethanol uptake.

Dynamic Study Temperature has a significant effect on adsorption capacity of an adsorbent (Slejko 1985). The dynamic study of water or ethanol uptake was done by varying temperature from 5 – 60 °C. Each sample contained 4 g of canola meal mixed in 150 g of pure water or pure ethanol solutions. The water and ethanol uptakes of canola meal were determined at specific time interval. The results of water uptake at different temperature are shown in Figure 2.

It was determined that the water uptake at all the tested temperatures increased rapidly with time, achieved over 90% of the equilibrium uptake during the first 30 min, and reached equilibrium at about 2 hrs. The results are quite similar to water uptake by cellulosic barley straw (Sun et al. 2007). Canola meal contains 20% neutral detergent fiber consisting of cellulose, hemicellulose and lignin (Canola Council of Canola 2009). Water uptake occurs between water molecules and polar groups in canola meal. This physical adsorption is fast. In addition, by increasing the temperature from 5 to 60 °C, water adsorption was rapidly increased for the first 30 min. However, highest

equilibrium water uptake was achieved at 25 °C among the tested temperatures. The equilibrium water uptake decreased as follows: 25 °C > 40 °C > 60 °C > 5 °C, indicating the water uptake at 25 – 60 °C may be exothermic.

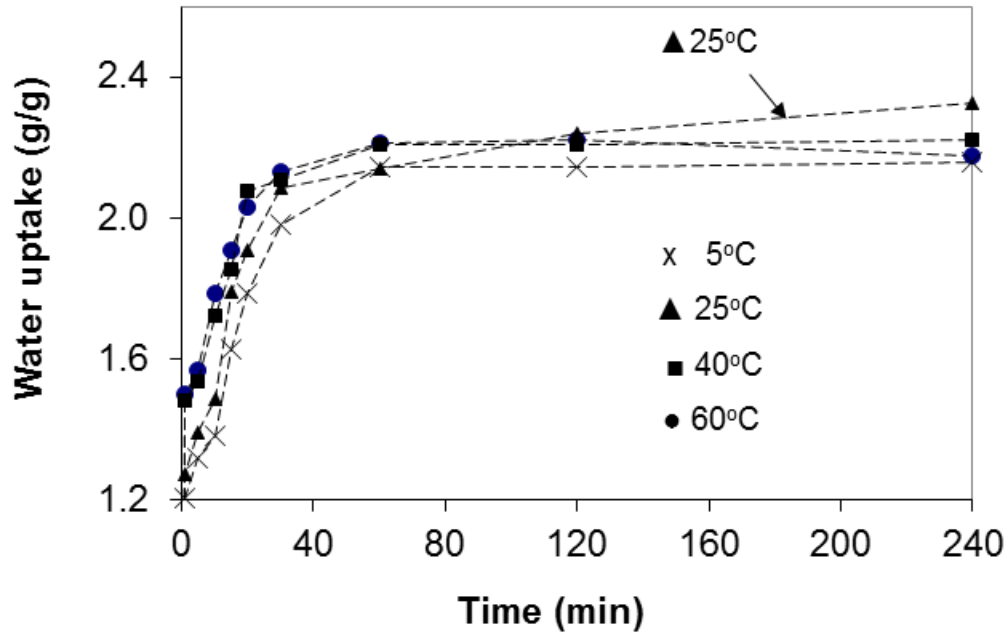


Figure 2. Dynamic study of water adsorption at difference temperature

Each sample contained 4 g dry adsorbents and 150 g pure water solution. The particle sizes of canola meal adsorbents were 1.18 – 3.35 mm.

The results are also similar to that obtained in ethanol-water liquid system using barley straw as biosorbent (Sun et al. 2007) in which water uptake was favored at 25 °C among the tested temperature range of 5 – 60 °C. At 5 °C, the structure of cellulosic components in canola meal is dense which makes it difficult for water molecules to access the sites in canola meal, thus uptake is low.

The effect of temperature on ethanol uptake is shown in Fig. 3. Similarly, as the temperature increased the ethanol uptake increased for the first 30 min. However,

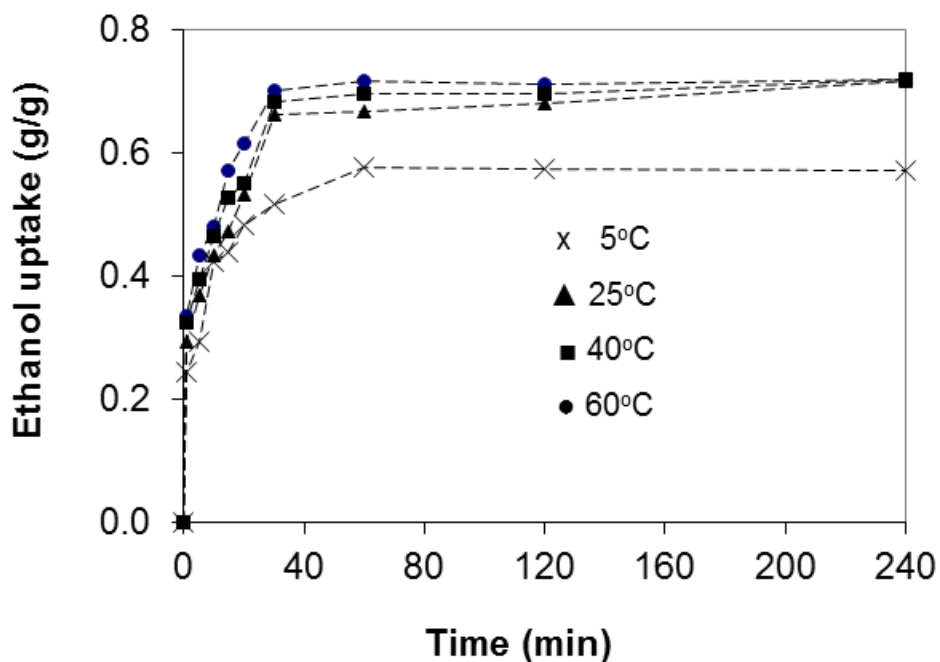


Figure 3. Dynamic study of ethanol adsorption at difference temperature

Each sample contained 4 g dry adsorbents and 150 g pure ethanol solution. The particle sizes of canola meal adsorbents were 1.18 – 3.35 mm.

equilibrium ethanol uptake almost reached the same value at 25 °C, 40 °C, and 60 °C, while being lower at 5 °C. Again over 90% of equilibrium ethanol uptake was achieved at the first 30 min and reached equilibrium at about 2 hrs. The mechanism of ethanol uptake by canola meal is not clear. It might be caused by diffusion of the relatively large ethanol molecule into the pores of the biomaterial particles followed by physical entrapment. Again ethanol molecule was not able to successfully access the adsorption site because of dense structure of canola meal at 5 °C. Water uptake by canola meal is constantly higher than ethanol uptake at the tested temperature range, demonstrating canola meal has higher water adsorption capacity over ethanol. Since over 90 % of equilibrium water or ethanol uptake was achieved within the first 30 min and the uptake increased at a slow rate before reaching equilibrium, contact time of 30 min was technically considered for the following pseudo-equilibrium experiments.

Pseudo-Equilibrium Isotherm To study the capacity of canola meal to adsorb water from a water-ethanol mixture, water and ethanol uptakes of canola meal were determined in water solution containing 0 –100% ethanol at 25 °C for 30 min which was considered as pseudo-equilibrium. The results are shown in Figure 4. It was found that water uptake by canola meal particles increased by increasing water concentration in the ethanol-water mixture. This demonstrates the ability of canola meal biosorbent to adsorb water from ethanol-water mixture with a wide range of water concentration (4 -100 wt %). Fig.4 also shows that canola meal particles are able to adsorb ethanol in a mixture containing 5.3 – 100 wt% ethanol. However, the maximum ethanol uptake (0.68 g/g) is much lower than that of water (2.08 g/g). The water uptake is constantly higher than that of ethanol in the tested ranges.

Canola meal consists of multi-components (Canola Council of Canola 2009). For a heterogeneous surface, a classical isotherm is the Freundlich isotherm (Perry et al. 2008). The isotherm corresponds approximately to an exponential distribution of heats of adsorption. Although it lacks the required linear behavior in the Henry's law region, it can often be used to correlate data on heterogeneous adsorbents over wide ranges of concentration. Freundlich equation was defined as follows:

$$q_e = K_f \cdot C_e^n \quad (2)$$

where q_e and C_e are equilibrium sorbate concentration on the adsorbent surface (g/g) and in the solution (wt%), respectively. K_f is the Freundlich constant related to the binding capacity of sorbent for sorbate (g/g) and n the affinity. In this work, K_f and n are determined by nonlinear regression of Equation (2). The optimal combination of parameter sets in the above model was obtained by minimizing the objective function error:

$$err = \sum \left(\frac{q_{\text{exp}} - q_e}{q_{\text{exp}}} \right)^2 \quad (3)$$

where q_{exp} and q_e are the experimentally obtained and the model calculated uptakes, respectively (g/g).

The model results are shown in Figure 4 and Table 2. It can be seen that Freundlich equation provided acceptable simulation to both water and ethanol isotherms. The coefficients of determination r^2 were above 0.97, and the standard errors of the estimate were less than 0.10. Either Langmuir model or Langmuir-Freundlich did not provide satisfied results. The obtained water adsorption isotherm being convex upward throughout indicates that water adsorption is favorable and the ethanol adsorption isotherm is concave upward throughout indicates ethanol adsorption is unfavorable. (Perry et al. 2008) The results are different from water / ethanol adsorption by barley straw, in which Langmuir-Freundlich model gave the best fit to water isotherm, and none of above models fit the ethanol isotherm. Since the composition of canola meal is different from that of barley straw, their adsorption behaviors are different.

The water uptake of 2.08 g/g dry canola meal achieved in this liquid system is much higher than that of the 3A molecular sieves (MS) (0.18 - 0.25 g water/g MS), which is commonly used in industrial ethanol dehydration process (Simo et al. 2009; Carmo and Gubulin 2006). It is also higher than water uptake by canola meal (0.16 g/g) from an ethanol-water vapor mixture in a pressure swing adsorption process (Baylak et al. 2012) which was affected by the process parameters such as temperature, pressure, and feed flow rate. Barley straw has a water uptake of 6.66 g/g and ethanol uptake of 2.81 g/g (Sun et al. 2007) in ethanol-water liquid mixture at the similar experimental conditions, which are respectively higher than that of canola meal (2.08 g water/g and 0.66 g ethanol/g). As a result, the molar ratio of water to ethanol uptake by canola meal of 8.1 is higher than that of barley straw 6.1. In order to quantify the selectivity of water over ethanol uptake, a separation factor was defined as (Baylak, et al., 2012),

$$\alpha = \frac{X_w / X_e}{Y_w / Y_e} \quad (4)$$

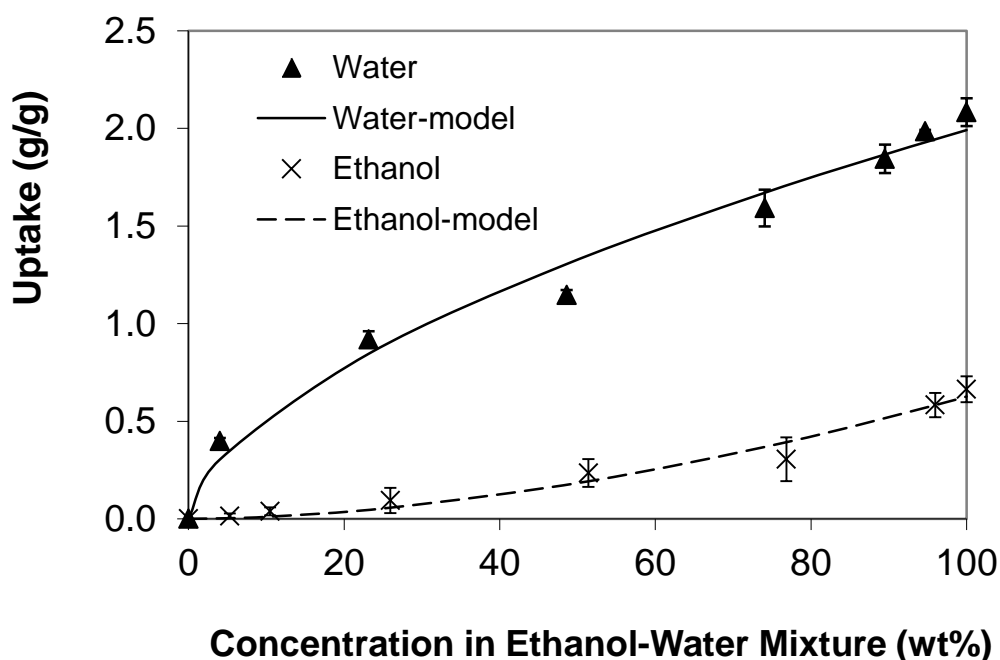


Figure 4. Pseudo-equilibrium adsorption isotherms of water and ethanol

Samples were run at 25 °C for 30 min. Each sample contained 4 g dry adsorbents and 150 g solution. Error bars represent 95% confidence interval.

where X_w and Y_w are the mass fraction of water in the adsorbed phase and liquid phase, respectively, and X_e and Y_e are the corresponding ethanol mass fraction. The separation factors were determined to be in the range of 5-16 according to specific equilibrium water-ethanol concentration in the liquid phase. The values are higher than that obtained by canola meal for ethanol-water vapor adsorption being 2-3 (Baylak et al. 2012). No results on separation factors of other adsorbents under the same experimental conditions were reported. Thus further comparison was not made. The water saturated canola meal was regenerated by oven dried at 105 °C for 24 hrs and was reused for adsorption.

CONCLUSION Canola meal was able to selectively adsorb water from ethanol-water liquid mixture in a wide range of water concentration from 4 to 100 wt%. Water uptake is constantly higher than that of ethanol. Over 90% of equilibrium water or ethanol uptake was achieved within the first 30 min. Water and ethanol uptake were associated with the specific surface area of the canola meal particles. Optimum water uptake was achieved at 25 °C. The pseudo-equilibrium isotherms of water or ethanol uptake were reasonably well fit by Freundlich equation. The water saturated canola meal was easily oven dried and reusable. The results demonstrated that canola meal has a potential for ethanol dehydration.

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NOMENCLATURE

C_0	Initial concentration of sorbate in liquid phase (wt %)
C_t	Concentration of sorbate in liquid phase at time t (wt %)
C_e	Equilibrium sorbate concentration in liquid phase (g/g solution)
K_f	Freundlich constant related to the binding capacity of sorbent for sorbate
n	Freundlich constant related to affinity of sorbent to sorbate
q_e	Calculated equilibrium sorbate uptake by Freundlich model (g/g dry adsorbent)
q_{exp}	Experimental sorbate uptake (g/g dry adsorbent)
X_e	Mass fraction of ethanol in the adsorbed phase
X_w	Mass fraction of water in the adsorbed phase
Y_e	Mass fraction of ethanol in the liquid phase
Y_w	Mass fraction of water in the liquid phase
w	Dry net biosorbent weight (g)
W_0	Weight of solution at initial condition (g)
W_t	Weight of solution at time t (g)

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