

## Adsorption of Water/Glucose Mixture onto Amberlite Resin

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The capacity of glucose removal in aqueous solution using Amberlite XAD4® was investigated. Experimental adsorption isotherm glucose onto Amberlite was carried out at 303 K and kinetic adsorption at 303 and 323K were performed in a batch reactor for 48 hours. The glucose concentration data were measured with ultraviolet-visible spectroscopy. To correlation the equilibrium data was use Freundlich, Toth, and Langmuir isotherms and to describe the kinetics data were use the pseudo-first-order and pseudo-second-order models. The result showed that resin has low effectivity at removal glucose in aqueous solution.

### 1. Introduction

Several industries require separation or removal steps of compounds of interest from a mixture. One example is the hydrolysis process employing gamma-valerolactone (GVL) and water as solvents to carbohydrate production such as glucose and xylose from biomass. Although a liquid-liquid separation process is necessary to decrease the quantity of GVL, a large amount of GVL remains in solution (Luterbacher et al., 2014). Among the separation techniques, the liquid phase adsorption is a common alternative approach to separate mixtures and it might be used in this process.

Many works, using adsorption to remove organic compounds from liquid phase, can be commonly found on the literature as can be seen on Bousba and Meniai, 2014 and Parisi et al, 2007; other works also used adsorption to remove glucose from liquid phase, such as Gramblicka and Polakovic (2007), Lei et al (2010), and Kuhn et al. (2012).

Thus adsorption is a complementary proposal to decrease the GVL in solution, after liquid-liquid extraction, since this solution may be used in other processes, for example, for ethanol production by a fermentation process.

High concentrations of GVL are toxic to the microorganisms that produce ethanol (Luterbacher et al., 2014), thereby it becomes important to remove the greatest possible amount of GVL from solution with the goal of improving the fermentation.

Before the present work, a test was performed with the actual solution to know the absorption with all compounds in the mixture. The present work is a preliminary adsorption study, since the adsorption of binary solutions is important in understanding the behavior of multicomponent mixtures on an adsorbent.

The main objective of this work was to perform glucose adsorption by a commercial resin Amberlite XAD4® (XAD4) and to obtain information about the process adsorption, such as equilibrium and kinetics aspects, to find out if it is a friendly alternative to prepare the fermentation solution to produce ethanol.

## 2. Experimental section

### 2.1 Materials

The adsorbate used was a glucose/water solution. It was used deionized water and D-glucose produced by Sigma Aldrich (99%). The adsorbent was Amberlite XAD4<sup>®</sup>, commercial resin produced by Sigma Aldrich.

### 2.2 Isotherm data

All of the equilibrium assays were carried out during 48h in test tube with cover containing 20mL of solution and 0.2g of resin. The solution was left to reach equilibrium in orbital shaker at 303 K with rotation speed of 100 rpm. The glucose solutions with initial concentration ranged from 1g/L to 30g/L were used to make the isotherm.

In this case, the initial and final sample solutions were collected to determine the concentration. The adsorbed glucose amount was determined by mass balance.

### 2.3 Kinetic data

The experiments were performed in batch reactor with 750 mL of glucose solution at 303 and 323 K and stirred at 100 rpm. The glucose concentration used 30g/L to 303 K and 27 g/L to 323K. We took 0.4 mL of solution on each sample.

The amount of adsorbed glucose  $q(t)$  at different time  $t$ , was calculated as follows:

$$q(t) = \frac{V(C_0 - C(t))}{M} \quad (1)$$

Where  $V$  is the volume of solution,  $C_0$  is the initial concentration of glucose in solution,  $C(t)$  is the concentration of glucose in solution on time  $t$ , and  $M$  is the adsorbent mass in dry base.

### 2.4 Analysis

Synthetic solution: The glucose concentration was determined by ultraviolet visible spectroscopy (Spectro Vision Model UV-vis SB-1810S, Shimadzu) at 505nm. The method used to determined was enzymatic method, glucose-oxidase, (Buttler et al., 2001) produced by Analysa. Linear calibration curve was constructed on 5 points with different concentrations (0.1; 0.5; 1; 2 and 3 g/L). The samples were analysed using 30 $\mu$ L of each sample in 3mL of Glucose-oxidase. All kinetic and equilibrium experiments were carried out in duplicate.

Actual solution: The actual solution with all compounds (Water/GVL/Glucose/Xylose) was used to test XAD4 behavior. In this test it was used 1g of resin in 10ml of solution, temperature 298.15K, under shaking for 10 min. The method used to analyze the actual solution is described in Luterbacher et al. (2014).

### 2.5 Mathematic models

#### 2.5.1 Isotherm Modeling

The adsorption isotherm equation used the equation 2,3 and 4. The Langmuir and Freundlich isotherms are the most used to represent the adsorption equilibrium. The Langmuir isotherm model is physically consistent and it considers that the active sites distributed on the surface of the adsorbent are homogeneous and there is no interaction between molecules of the adsorbent. The Langmuir isotherm can be described by:

$$q_{eq} = \frac{q_m C_{eq}}{1 + b C_{eq}} \quad (2)$$

where  $q_m$  and  $b$  are the adjustable parameters.

The Freundlich isotherm can be represented in the following form:

$$q_{eq} = k C_{eq}^n \quad (3)$$

where  $k$  and  $n$  are the adjustable parameters.

The main restriction of this model is that it does not provide the active sites saturation, so it should only be used in the concentration range in which its parameters were adjusted.

Toth proposed an equation based on the equation of Langmuir for in order to improve the model fit the experimental data. It gives better results when applied to multilayer adsorption (Khan et al, 1997). Toth's equation is represented by the following equation:

$$q_{eq} = \frac{q_m C_{eq}^n}{(b + C_{eq}^n)^{1/n}} \quad (4)$$

where  $n$ ,  $q_m$ , and  $b$  are the adjustable parameters

### 2.5.2 Kinetics Modeling

Computational simulation was performed with two models pseudo-first-order and pseudo-second-order model. Both models are a mathematically expressed by the differential equations, respectively:

$$\frac{dq}{dt} = k_1 (q_{eq} - q) \quad (5)$$

$$\frac{dq}{dt} = k_2 (q_{eq} - q)^2 \quad (6)$$

where  $q(t)$  is the amount adsorbed at time  $t$ ,  $q_{eq}$  is the amount adsorbed at equilibrium,  $k_1$  and  $k_2$  are the pseudo-first and pseudo-second-order kinetic rate parameter, respectively, integrating the equations (5) and (6) on range of 0 to  $t$  and 0 to  $q$ , it become:

$$q(t) = q_{eq} (1 - e^{-k_1 t}) \quad (7)$$

$$q(t) = \frac{k_2 (q_{eq})^2 t}{1 + k_2 q_{eq} t} \quad (8)$$

where equation (7) is an explicit equation for  $q(t)$  to pseudo-first-order model and the equation (8) is an explicit equation for  $q(t)$  to pseudo-second-order model.

The second-order model is based on the adsorption capacity inside solid phase. In contrast the first-order is a model to predict the adsorption behaviour over a wide range and it is consistent with a mechanism such as adsorption rate controlling step. If the rate of adsorption is expressed by a second-order, the pseudo-second-order of chemisorption can be applied for each component in the mixture (Aksu and Gulenm, 2002).

## 3. Results and Discussions

### 3.1 Actual Solution

Table 1 presents the results from the analysis of the actual solution obtained by the hydrolysis of corn stover, with the initial values of each component (Feed) and the final values of each component after adsorption by 1g of XAD4. The hydrolysis was done according to the same procedure presented by Luterbacher et al. (2014).

Table 1: Adsorption experimental data of the actual aqueous solution

Components	Feed (mol/L)	Adsorption (mol/L)
GVL	0.2717	0.1660
Glucose	0.3687	0.2760
Xylose	0.2776	0.3676

The results showed a higher adsorption of GVL from the liquid phase than Glucose. Therefore, it is important to know the adsorption behavior of the Glucose/Water solution on the resin, since Glucose may have a different rate of adsorption or a different adsorption time compared with GVL.

### 3.2 Kinetics

In Table 2, the model parameters, obtained using least squares regression analysis, are reported together with the correspondent determination coefficient ( $r^2$ ).

Table 2: Kinetic parameters fitted to experimental data

Model	T/K	Parameter	$r^2$
Pseudo-first-order		$k_1 / \text{min}^{-1}$	
	303	$2.9310 \cdot 10^{-3}$	0.9873
	323	$5.5920 \cdot 10^{-2}$	0.9582
Pseudo-second-order		$k_2 / \text{g.mg.min}^{-1}$	
	303	$5.9222 \cdot 10^{-6}$	0.8810
	323	$1.6864 \cdot 10^{-4}$	0.9151

The amount of glucose adsorption onto resin have been plotted as function of time  $t$  in minutes under two different temperature which shown in Figure 1.A and Figure 1.B. Both cases showed that  $q(t)$  increased with a time increase until it reaches equilibrium adsorption. According to the statistical analysis of the correlation coefficient, the model with the best fit was the pseudo-first-order model.

The results showed that the adsorption kinetics is slow and it was affected by temperature. The equilibrium time was reached around 1500 min, for 303K experiment, while the temperature 323K the time was around 750min. The parameters model results are consistent with the temperature effect, because the parameter value is directly proportional with rate adsorption. Kuhn et al (2012) used cationic zeolite for glucose adsorption and the equilibrium time was reached about 100min. This shows that the adsorbent of them was a better glucose adsorbent compared to this study, but it is not interesting to our process.

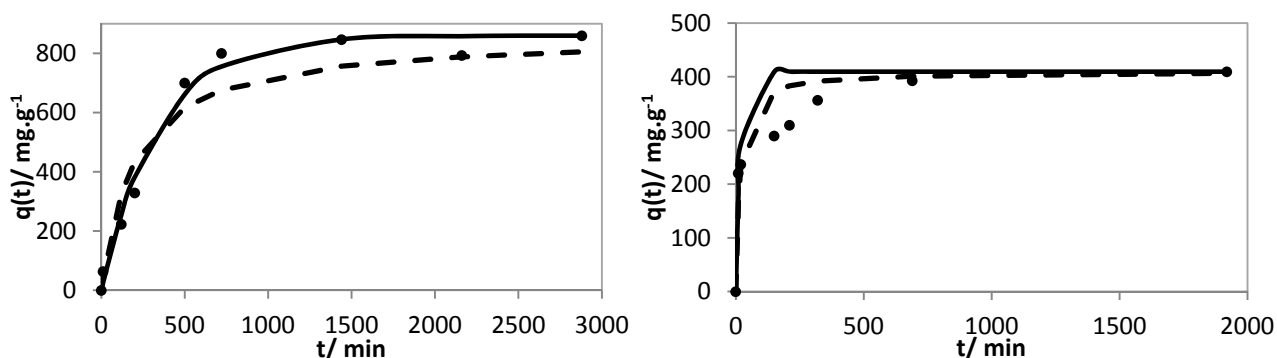


Figure 1.A: Relationship of  $q(t)$  vs. time for the adsorption at 303K Figure 1.B: Relationship of  $q(t)$  vs. time for the adsorption at 323K, ● experimental data  
— pseudo-first-order, - - - pseudo-sec.-order,

The Table 2 results showed that increasing temperature also increases the kinetic constant. This fact may result from increased adsorbate diffusion onto resin, which occurs with increasing temperature. According to the computer simulation, the model that obtained the best fit was the pseudo-first-order model.

### 3.3 Isotherm

Parameter fitting to isotherm also was performed with least squares to three isotherms models: Langmuir, Freundlich, and Toth. For Langmuir model, the coefficient  $r^2$  was shown to be lower than the other models, as shown in Table 3, so that it has low representation, in this case. The behavior of equilibrium data has showed that isotherm is not favorable to glucose adsorption. However, the adsorption process is suggested when the adsorbent has high adsorption capacity, even at low concentration of the interest compound in liquid phase.

Table 3: Isotherm parameters fitted to experimental data

Model	Parameters			$r^2$
Langmuir	$q_m$	$b$		0.9437
	2250.44	$5.9509 \cdot 10^{-6}$		
Freundlich	$k$	$n$		0.9642
	$1.7998 \cdot 10^{-4}$	1.4239		
Toth	$q_m$	$n$	$b$	0.9660
	$9.5688 \cdot 10^4$	2.2538	11.8737	

The experimental results along with the adjustment of the models have been shown in Figure 2.

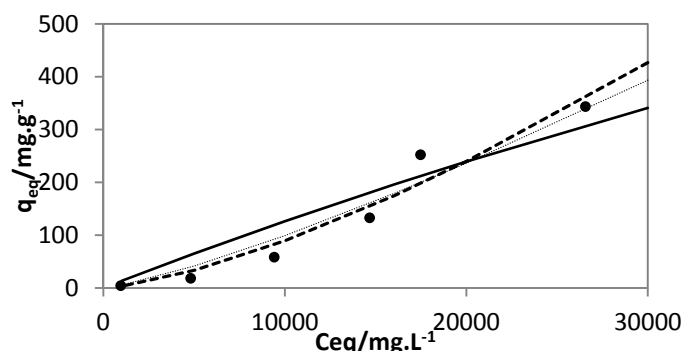


Figure 2: Relationship of  $q_{eq}$  vs. glucose concentration in equilibrium adsorption at 303K, ● exp. Data, --- Freundlich, .....Toth, and — Langmuir.

As can be seen from Figure 2, the best fit was achieved with Freundlich and Toth models. In this case it means that the behaviour of the resin is multilayer adsorption for water-glucose, since these two models have this kind of behaviour.

Lei et al (2010) evaluated the adsorption of glucose using gel-type strong-acid cation exchange and concluded that at low concentrations, the isotherm has a linear behavior. Such behavior has been studied by Gramblicka and Polakovic (2007) in the adsorption of sucrose.

#### 4. Conclusions

In this work we studied the effects of glucose adsorption on to Amberlite XAD4<sup>®</sup>, a commercial resin. Since the glucose is the compound of interest, the resin adsorbs a low glucose amount, and needs a high time to reach equilibrium, i.e. the adsorption is not favourable. Our results revealed that the resin Amberlite XAD4<sup>®</sup> is effective for the hydrolysis process using GVL, because the main process goal is to remove GVL instead of glucose.

Although this resin presented these glucose adsorption results, it is still necessary to evaluate the resin behavior with GVL/water and GVL/Glucose/water, so future research will be necessary to study the desorption kinetics of all compounds to conclude that our proposed approach could become a viable alternative to remove GVL from the solution to further produce ethanol from the fermentation of glucose.

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## References

- Aksu Z., Gülenm H., 2002. Binary biosorption of iron(III) and iron(III)-cyanide complex ions on *Rhizopus arrhizus*: modelling of synergistic interaction, *Process Biochemistry*, 38, p. 161-173
- Bousba S., Meniai A. H., 2014, Removal of Phenol from water by adsorption onto sewage sludge based adsorbent, *Chemical Engineering Transactions*, 40, 235-240, DOI: 10.3303/CET1440040
- Butler M. A., Vanýsek P., Yamazoe N., 2001, "Chemical and biological sensors and analytical methods II: proceedings of the international symposium". The Electrochemical Society. ed. 18. p. 223
- Gramblicka M., Polakovic M. 2007. Adsorption Equilibria of Glucose, Fructose, Sucrose, and Fructooligosaccharides on cation Exchanges Resins. *J. Chem. Eng. Data*, 52, p. 345-350.
- Khan A. R., Ataullah R., Al-Haddad A. 1997. Equilibrium Adsorption Studies of Some Aromatic Pollutants from Dilute Aqueous Solutions on Activated Carbon at Different Temperatures, *J. Colloid Interface Sc.*, v.194, p. 154–165.
- Kuhn R. C., Mazutti M. A., Mauger Filho F., 2012, "Kinetic and Transfer effects for adsorption of glucose, fructose, sucrose and fructooligosaccharides into X zeolite. *LWT – Food Science and Technology*, 48, p. 127-133.
- Lei H., Bao Z., Xing H., Yang Y., Ren Q., Zhao M., Huang H., 2010. "Adsorption behavior of glucose Xylose, and Arabinose on Five Different Cation Exchange Resins" *J. Chem. Eng. Data*, 55, p. 735-738.
- Li, Q., Yue, Q. Y., Su, Y., Gao, B. Y., & Li, J. 2009. Two-step kinetic study on the adsorption and desorption of reactive dyes at cationic polymer/bentonite. *Journal of hazardous materials*, 165(1), 1170-1178.
- Luterbacher J.S.; Rand J.M.; Martin Alonso D.; Han J.; Youngquist J.T.; Maravelias C.T.; Pfleger B.F.; Dumesic J.A. 2014, Nonenzymatic Sugar Production from Biomass Using Biomass-derived  $\gamma$ -Valerolactone. *Science*, 343, 277-280. (DOI: 10.1126/science.1246748)
- Martins T. D., Schimmel D., Santos J. B. O., Silva E. A., 2013, Reactive blue 5G adsorption onto activated carbon: kinetics and equilibrium. *J. Chem. Eng. Data*, 58, 106–114
- Parisi M., Festuccia A., Chianese A., 2007, Polyphenols recovery from wastewater by polymeric resins, *Chemical Engineering Transactions*, 11, 185-190, ISBN: 978-88-95608-00-6