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Effect of Agitation on Removal of Acetic Acid from Pretreated Hydrolysate by Activated Carbon

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Abstract

The effect of agitation on the adsorption of acetic acid by activated carbon was tested utilizing an external mass transfer–diffusion model. Simulated pretreated biomass was contacted with activated carbon under prescribed conditions of temperature and agitation. Adsorption isotherm studies are presented as well as batch kinetic rate studies. Use of these data enabled the determination of isotherm constants, an external mass transfer coefficient, and an effective diffusivity for each agitation rate studied. The external film coefficient results ranged from 33.62 μm/s to a complete absence of external mass transfer resistance, and the diffusivity results ranged from 0.8625 to 10.70 $\mu m^2/s$. The optimum combination of no external film resistance, and highest diffusivity, 10.70 $\mu m^2/s$, occurred at 250 rpm and 25°C. The results of these models and the experimental parameters suggested an efficacious method and conditions for the removal of this undesirable chemical.

Index Entries: Adsorption; activated carbon; external mass transfer; effective diffusivity; detoxification.

Introduction

Biomass sources such as softwoods and corn stover have been touted as viable solutions for the production of fuel ethanol. However, because these sources do not contain significant quantities of sugar in their natural state, they must be treated in a manner in which the lignocellulosic material is reduced to fermentable sugars. This is accomplished by any number of pretreatment processes such as dilute-acid hydrolysis *(1)*. During the pretreatment of most biomass systems, several components resultant from sugar and lignin degradation processes may be formed, including furfural, hydroxymethylfurfural, and acetic acid. The quantity of the individual chemicals can vary with biomass source and may range from parts per

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million to grams per liter. While most of these chemicals are never produced in great quantity, they impact the fermentation capability of the ethanologenic organisms, especially bacteria *(2)*. The impact of these inhibitory chemicals on fermentation yield has also been studied. In the case of the ethanologenic bacterium *Zymomonas mobilis*, concentrations of acetic acid found in pretreated softwoods may reach 10 g/L, completely inhibiting fermentative ability *(3)*.

To combat the problems associated with these inhibitory chemicals, several detoxification schemes have been investigated including treatment with alkali, sulfites, and ion exchange *(4–7)*. While these methods were able to remove some of the inhibitory components, little attention was paid to the potential of activated carbon adsorption. Activated carbon adsorptions provide process advantages such as ease of use and scale-up ability. They are regenerated easily with steam, and the stripped components may be collected and sold. In addition, powdered activated carbons are much less costly than ion-exchange resins. Activated carbon processes have been in use for more than 200 yr and are quite commonly used in the alcoholic beverage industries *(8)*. Activated carbons are produced by a wide variety of substrates and may be found in either granular or powered forms for use in both continuous and batch applications *(9)*.

In the present study, an activated carbon hydrolysate detoxification step was investigated. Following biomass pretreatment, the resulting hydrolysate was processed through a separation step. In this step, the hydrolysate substrate was contacted with an activated carbon under specific conditions of temperature, carbon concentration, composition, and agitation. To avoid issues associated with biomass inconsistency, acetic acid was added synthetically at predetermined levels. Through isotherm and kinetic rate testing, key parameters were determined and applied to a mathematical model. This model allowed determination of the external mass transfer coefficient and the effective diffusivity. These mass transfer parameters then permitted evaluation of the carbon treatment process *(10)*.

Materials and Methods

Isotherm and Activated Carbon Kinetic Rate

For isotherm testing and activated carbon kinetic rate testing, activated carbon manufacturers were contacted and asked to supply samples of carbon that may effectively remove acetic acid from a water-based medium. Two carbon manufacturers, Calgon Carbon (Pittsburgh, PA) and Carbon Resources (Oceanside, CA), responded and supplied samples. Each sample was deemed by its respective manufacturer to be effective under the previously described process conditions. Calgon Carbon supplied two products: BL pulverized and PWA powdered. Carbon Resources provided four carbon products of varying origin. CRWCA, 2SAP, CR325BP, and CRCNSP-60. A summary of commercially available activated carbons, including those tested, is given in Table 1.

Table 1
Classifications of Commercially Available Carbons

Carbon source	Commercial example
Bituminous coal	Calgon BL and PWA, Carbon Resources CR325BP
Coconut shell	PICA USA G216, Carbon Resources CRCNSP-60
Wood	Darco KB, Carbon Resources CRCWA and 2SAP
Lignite	Darco S

An Innova Model 4230 benchtop refrigerated incubator/shaker from New Brunswick Scientific (Edison, NJ) was used for the adsorption isotherm experiments. The incubator has stainless steel shelves and an Erlenmeyer flask platform capable of holding twenty-five 250-mL flasks. Microprocessor controls maintain speeds ranging between 25 and 400 rpm and temperatures from 20°C below ambient temperature to 80°C.

For each carbon and condition tested, seven 250-mL Erlenmeyer flasks were cleaned and dried. One hundred milliliters of the isotherm medium consisting of 10 g/L of acetic acid in deionized water was added to each flask. The predetermined activated carbon amount was then added to each flask: 10, 20, 40, 60, 80, or 100 g/L. The flasks were covered with Parafilm to prevent evaporation. The flasks and two different controls (medium without carbon and water with carbon) were placed in the refrigerated incubator/shaker set at a controlled agitation rate and temperature (200 rpm, 15°C). The adsorption isotherm study was allowed to proceed for 24 h, at which point the flasks were removed from the shaker. The carbon was allowed to settle for a short period of time and the medium was then filtered with a 0.2-μm syringe filter to remove the remaining carbon fines. The isotherm samples were then titrated with standard alkali to determine acetic acid content.

Adsorption Kinetics

A 4-L reaction kettle was used for the adsorption kinetic testing. The reactor consisted of a glass housing and one stainless steel R100 impeller held on a central stainless steel agitation shaft. A Lightnin mixer with digital-rotations-per-minute indicator provides the agitation. Samples were withdrawn through a port in the vessel cover. A diagram of this apparatus is provided in Fig. 1.

With the impeller operating at the desired rate and the vessel at the desired temperature, the selected activated carbon was carefully introduced into the medium through a port in the reaction vessel cover at time zero. Samples were removed at predetermined time intervals (2 min) though the same port and were immediately filtered with a 0.2-μm syringe filter to remove the activated carbon and to stop the adsorption process. The samples were then titrated with standard alkali to determine the acetic acid concentration. These steps were repeated for each tested condition.

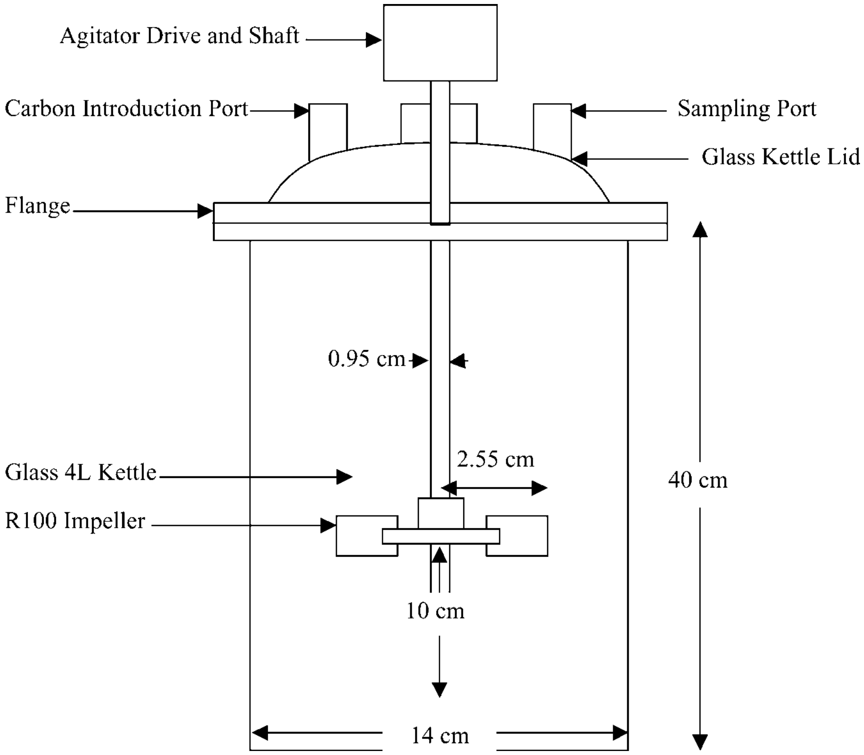

Fig. 1. Diagram of reaction kettle.

Model

To describe the adsorption rate data, a mathematical model must be developed. This model incorporates a method for determining the two major factors affecting adsorption: external mass transfer and diffusivity. These two factors play an important role in the design and scale-up of adsorption equipment.

To supply information for the model, data are collected at predetermined time intervals during the kinetic portion of experimentation as previously described. The initial fraction of the plot obtained is then interpreted using a four-step mechanism. In this mechanism, only the initial data, <10 min, are used owing to the presence of a linear isotherm during this time period. The four-step mechanism is as follows: (1) mass transfer of solute through bulk solution, (2) mass transfer from bulk solute to particle surface, (3) intraparticle diffusion, and (4) adsorption on an interior site. If a solution is well mixed, no concentration gradients will exist within the bulk solution and the bulk diffusion term may be ignored. It can also be assumed that adsorption on an interior site is rapid with respect to the remaining two steps *(11)*. In the initial phases of adsorption, external mass transfer is the controlling mechanism. As time progresses or as agitation rates increase, external mass transfer plays a smaller role and intraparticle diffusion begins to dominate the adsorption process. To calculate the external mass transfer coefficient the following equations are used *(11)*:

$$\frac{dC_b}{dt} = \frac{-3k_f m\,(C_b - C_s)}{R\rho_s(1-\varepsilon)} \tag{1}$$

$$\left(\frac{C_b}{C_{bo}}\right) = \frac{1}{1+mK} + \frac{mK}{1+mK}\exp\left(-\left[\frac{1+mK}{mK}\right]\left[\frac{3k_f mt}{R\rho_s\{1-\varepsilon\}}\right]\right) \tag{2}$$

Eq. 1 is the result of a differential mass balance on the carbon particle, solved in Eq. 2 for the limiting case of a linear isotherm

$$KC_s = \left(\frac{C_{bo} - C_b}{m}\right)$$

A linear isotherm has been validated for this system for contact times of <10 min.

The effective diffusivity is then determined. Although diffusivity terms include bulk, surface, and intraparticle diffusivities, these individual parameters are difficult to determine. By calculating the effective diffusivity, all of the individual diffusivities are lumped into a single parameter that may be determined by observation of bulk fluid properties. A shell balance on the system for constant density and diffusivity is found in Bird et al. *(12)*. With no reaction, assuming no convection, and diffusion occurring only radially in the carbon particle, this equation reduces to Fick's law of diffusion, Eq. 3. The differential mass balance for this system can be seen in Eq. 4. Equation 4 has the following initial condition: at $t = 0$, $C_b = C_{bo}$ and $C = 0$ for $0 \le r \le R$:

$$\frac{dC}{dt} = D_e \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C}{\partial r}\right) \tag{3}$$

$$V_f \frac{dC_b}{dt} = \frac{-3W}{R\rho_s} D_e \frac{\partial(R,t)}{\partial r} \tag{4}$$

For an external mass transfer–controlled adsorption, Eq. 3 is subject to the following conditions:

Initial condition:

$$t = 0 \quad C = 0 \textit{ for } 0 \le r \le R$$

Boundary conditions:

$$t > 0 \quad \frac{\partial C}{\partial r}\Big|_{r=0} = 0 \quad \text{and} \quad D_e \frac{\partial C}{\partial r}\Big|_{r=R} = k_f\,(C_b - C_s)$$

Equation 5 allows determination of effective diffusivity *(13)*:

$$\frac{C_b}{C_{bo}} = \frac{1 + B\exp(-3\,[1+B]\,\tau)}{1+B} \tag{5}$$

For an intraparticle diffusion–controlled adsorption, Eq. 3 is subject to the following conditions:

Initial condition:

$$t = 0 \quad C = 0 \ \mathit{for} \ 0 \le r \le R$$

Boundary conditions

$$t > 0 \quad \frac{\partial C}{\partial r} \mid_{r=0} = 0 \ \text{ and } \ C = C_b \text{ at } r = R$$

This equation may be solved by a generalized Sturm-Liouville Integral transform, resulting in Eq. 6 *(14)*:

$$\frac{C_b}{C_{bo}} = \frac{B}{B+1} + 6B \sum_{n=1}^{\infty} \frac{exp\left(-\xi_n^2 \tau\right)}{\left(9 + 9B + B^2 \xi_n^2\right)} \tag{6}$$

in which the Eigenvalues are determined by Eq. 7:

$$\tan \xi_n \frac{3\xi_n}{3 + B\xi_n^2} \tag{7}$$

In all cases, the following assumptions are made: linear isotherm region, well-mixed bulk solution, sample times close to t_o, initially solute-free carbon pores, spherical carbon particles, and constant effective diffusivity. From these equations it can be seen that a plot of

$$\ln\left(\frac{C_b}{C_{bo}} - \frac{1}{1 + mK}\right)$$

vs t is linear with a slope of

$$-\left(\frac{1 + mK}{mK}\right) \frac{3mk_f}{R\rho_s\left(1 - \varepsilon\right)}$$

thereby allowing k_f to be calculated. In addition, since t and τ are related through the dimensionless variable, a plot of τ vs t should yield a straight line with a slope equal to D_e/R^2. The effective diffusivity may then be determined.

Results and Discussion

Results of the adsorption isotherm experiments are presented in Fig. 2. The data resulting from these experiments were fitted to a Freundlich isotherm model. Using this isotherm model, three items must be investigated to properly evaluate the activated carbons: isotherm slope, isotherm intercept, and final achievable substrate concentration. By directly comparing isotherms, the equilibrium effects of the activated carbon are revealed. For the case of acetic acid adsorption, a smaller slope indicates a decreased dependence on concentration and is therefore considered favorable. The highest possible intercept is also desired. This value indicates the capacity of the activated carbon. Finally, the lowest residual acetic acid concentration is

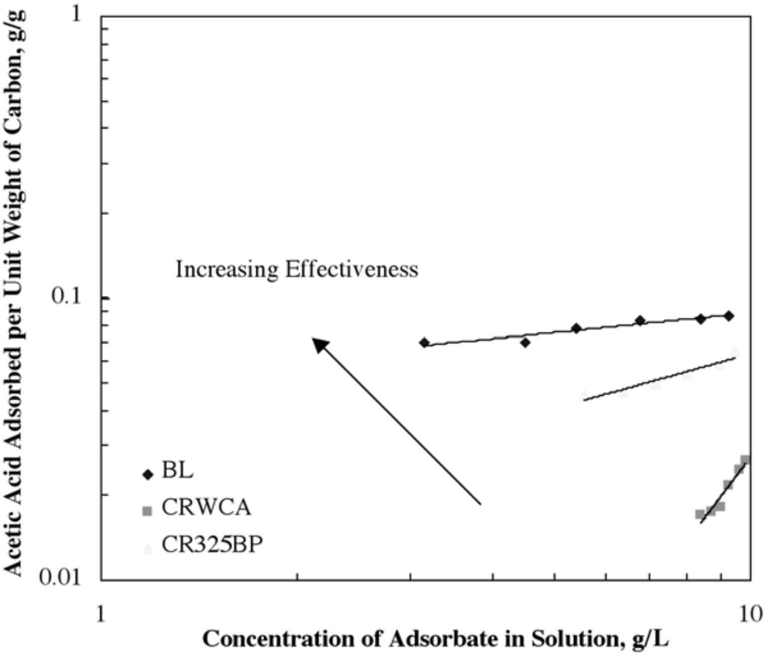

Fig. 2. Adsorption isotherm curve comparison for acetic acid at 15°C.

desired. When Calgon carbons and Carbon Resources carbons were compared on the adsorption of acetic acid, two of the tested carbons, Calgon BL and Carbon Resources 2SAP, performed the best. Each of these carbons had isotherm slopes at least 1.5 times smaller than the nearest competing carbon and isotherm intercepts 1.36 times larger than the other carbons. Both of these carbons were also capable of removing >67% of the initial acetic acid from solution at the 15°C reaction temperature. However, one aspect of activated carbon usage—cost—eliminated the Carbon Resources carbon. Therefore, utilizing the criteria mentioned previously (isotherm slope, isotherm intercept, and final substrate concentration) and cost factors, a single activated carbon was selected for further testing: Calgon Carbon BL at a usage rate of 80 g/L. Although not presented in graphic form here, isotherms for the adsorption of glucose were also performed. Calgon Carbon BL adsorbed the least amount of glucose from solution, approaching nearly 20% of the initial concentration. This amount of sugar is lost only in the pore volume of the carbon and is not actually adsorbed to the carbon surface. Even this level of sugar loss is considered unacceptable, future process modifications may decrease this loss.

Following the selection of an activated carbon, adsorption kinetic tests were performed using the 4-L reaction kettle shown in Fig. 1. The curves resulting from these tests as shown in Fig. 3. Two important pieces of information may be gleaned from this plot. First, the curves help determine the

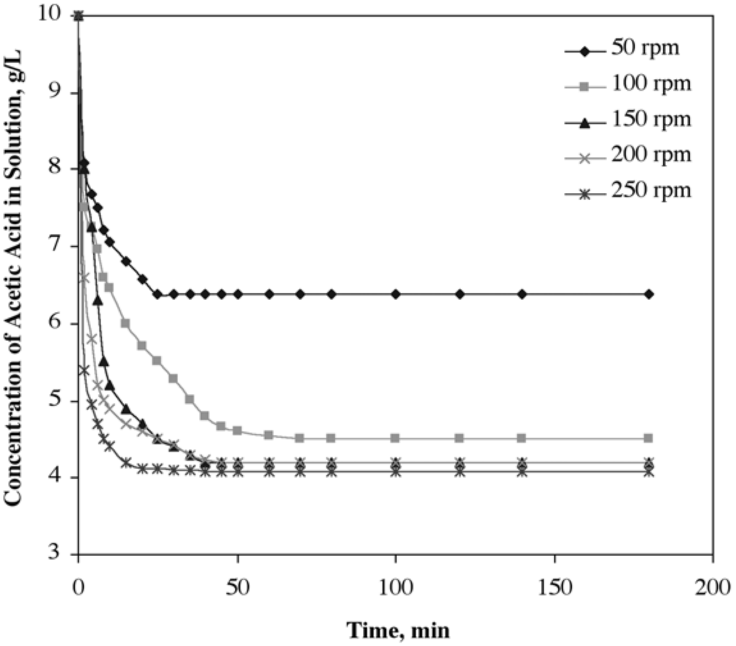

Fig. 3. Acetic acid concentration as function of time and rpm at 15°C using Calgon Carbon BL.

time required to reach equilibrium. Calgon Carbon suggested that the time required to reach equilibrium for this system would be >24 h. However, from these curves it can be seen that local equilibrium concentrations were reached in <30 min for all agitation rates and in as little as 20 min for the highest agitation rates. These fast equilibrium times may be attributed to the affinity of this carbon for acetic acid. Figure 3 also indicates final local equilibrium concentrations. Note that after a great amount of time passed (>48 h), the same equilibrium was achieved, and that the equilibrium recorded was a local, not a true, equilibrium. Clearly, the 50-rpm agitation rate does not perform well, achieving half of the equilibrium concentration of the remaining rates. This can be attributed to incomplete mixing of the carbon particles since it was observed that a quantity of carbon remained at the bottom of the reaction vessel at the end of the kinetic experiment. Equilibrium concentrations also were observed to decrease with agitation rate. This result was not originally expected but indicates that a controlling mass transfer resistance exists for the lower agitation rates and shows that the degree of agitation does indeed have an effect on the adsorption of acetic acid by activated carbon.

Having completed the kinetic studies, we applied the developed model to the collected data. The results of the model application are given in Fig. 4, describing the external mass transfer coefficient, and in Fig. 5, describing the effective diffusivity. The calculated values for the external

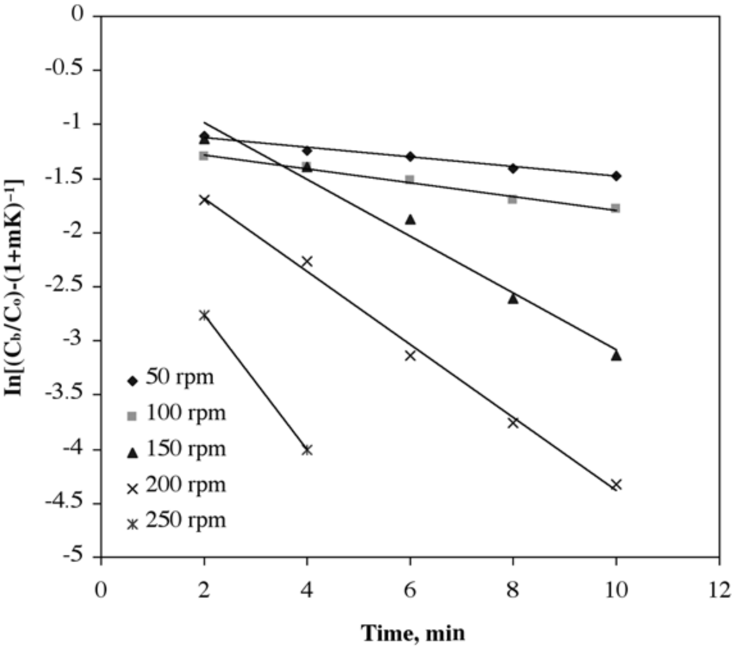

Fig. 4. Dimensionless external film coefficient term as function of time and rpm at 15°C using Calgon Carbon BL.

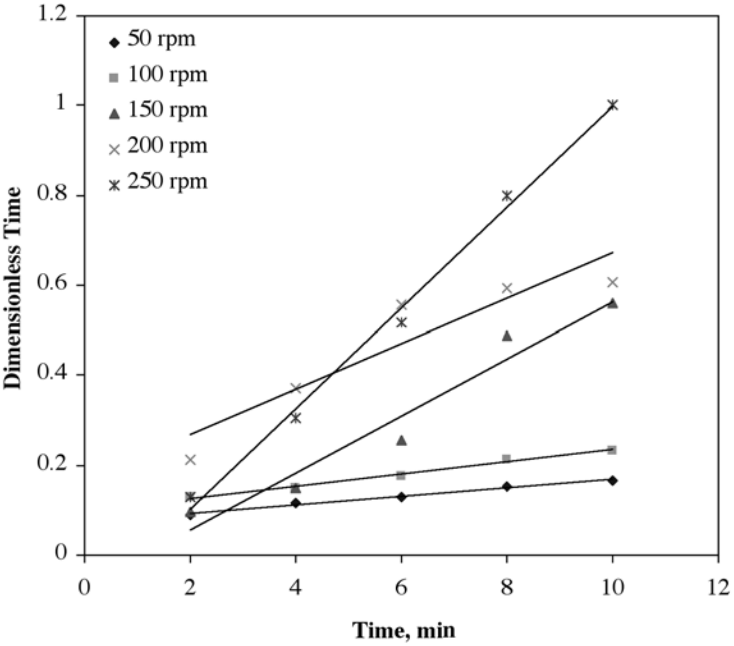

Fig. 5. Dimensonless time as function of time and rpm at 15°C using Calgon Carbon BL.

Table 2
Summary of Calculated Mass
Transfer Parameters at 15°C

rpm	k_f (m/s)	D_e (m^2/s)
50	3.577×10^{-8}	8.625×10^{-13}
100	4.996×10^{-8}	1.275×10^{-12}
150	2.056×10^{-7}	5.925×10^{-12}
200	2.642×10^{-7}	9.170×10^{-12}
250	ND[a]	1.049×10^{-11}

[a] Not determined.

mass transfer coefficient and the effective diffusivity are summarized in Table 2.

The overall trend that can be deduced from Fig. 4 is that the external film coefficient increases with increasing agitation rate. The difference between the 50- and 250-rpm agitation rate is nearly 640% at 15°C. Note that these studies uncovered an interesting occurrence in the mathematical model used to calculate the external mass transfer resistance: as concentrations began to approach equilibrium, one of the terms in the governing equation tended toward zero. A logarithm of this value then becomes undefined. This situation is encountered early in the 250-rpm agitation rate for 15°C, because at this rate equilibrium concentrations are approached in under the 10-minute process time and indicate the disappearance of any external mass transfer resistance. The end effect of these external mass transfer resistances is reflected in the effect of agitation on kinetic rate. As agitation increases, the external mass transfer coefficient also increases, indicating a decrease in resistance. This decrease in mass transfer resistance leads to the lower equilibrium concentrations seen in the 200- and 250-rpm agitation rates.

Based on the results of the external mass transfer coefficient experiments, both external mass transfer and intraparticle diffusion resistance modes are in effect at different periods during experimentation. When an external mass transfer coefficient can be reliably calculated, the model equations governing diffusion limited by external mass transfer are employed. This is the case for 50, 100, 150, and 200 rpm at 15°C. When an external mass transfer coefficient cannot be calculated because of the elimination of the external mass transfer resistance, intraparticle diffusion limits. This occurred in the 250 rpm, 15°C case. The overall trend that can be deduced from Fig. 5 is that diffusivity increases with increasing agitation rate. The difference between the 50 and the 250-rpm rate is nearly 1300% at15°C.

Overall, the process conditions of 15°C and 250 rpm using the Calgon Carbon BL provided the highest level of acetic acid adsorption with the highest effective diffusivity, the fastest mixing time, and in an environment free from external mass transfer resistance. All of the phases of experimentation can be combined to show that the final equilibrium concentration of the 250-rpm kinetic test was reflected in the final equilibrium concentrations found during adsorption isotherm testing. It can also be concluded that the linear models presented previously performed well in predicting the external mass transfer coefficient and the effective diffusivity. Both Figs. 4 and 5 show a high degree of correlation with the data and the applied linear model. However, all results found during our study are limited to the reactor size used during testing, and the data collected are not easily extrapolated to other systems. Scale-up issues for the pretreatment detoxification system were not investigated and are the subject of future research. Clearly, if this process were to be implemented, mixing and reactor characteristics would need to be studied.

Finally, the possibility of a combination detoxification and fermentation was not explored. Activated carbon, when added directly to the fermentation broth, could adsorb the detrimental acetic acid. This method could also reduce the amount of sugar removed from the system since the glucose was lost in the pore volume of the carbon. Glucose utilization by the fermenting organism would allow sugar trapped in this pore volume to diffuse back into the bulk solution for consumption. Additionally, while the temperature selected for this study was 15ºC, a 25ºC study was also performed but not presented here. Based on recommendations from the carbon manufacturers, the favorable results seen here suggest that an investigation into higher temperatures may be beneficial. Carbon treatment at the higher temperatures would reduce energy requirements for cooling the hydrolysate for detoxification and then heating it again for fermentation.

Conclusions

The results of the adsorption kinetic experiments are valid for 10 g/L acetic acid solutions, agitated by a Rushton turbine impeller at 50, 100, 150, 200, and 250 rpm in a 4-L glass reaction vessel, and contacted with 80 g/L of the powdered activated carbon Calgon BL at 15ºC. Equilibrium was achieved 24 times faster than the time recommended by the manufacturer of the activated carbon for this tested system. For 150, 200, and 250 rpm, >62% of the initial acetic acid was adsorbed. The presented model describing a linear approach to the external film resistance is supported with coefficients of correlation ranging from 0.93 to 0.99, and those describing a linear approach to the effective diffusivity are supported with coefficients of correlation ranging from 0.84 to 0.99.

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Nomenclature

B = capacity ratio = $1/mK$
C_b = bulk reservoir concentration (g/L)
C_{bo} = initial solute concentration (g/L)
D_e = effective diffusivity (m^2/s)
k_f = external mass transfer resistance (m/s)
K = linear isotherm constant
m = carbon dosage (g/L)
R = radius of a particle (m)
t = time (s)
ε = porosity
ρ_s = adsorbent solid density (kg/m^3)
τ = dimensionless time parameter = D_e/R^2

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