Kinetic Adsorption Study of Maltose Osmotic Agent onto Granular Activated Carbon in SET Technique

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Abstract

This paper presents the kinetic adsorption of maltose from aqueous solution onto granular activated carbon (GAC). Attempts have been conducted experimentally by shaking different GAC samples doses (5, 10 and 30 g/l) with 6000 mg/l maltose concentration solution for 8 hr at different shaking speed values (45,100 and145 rpm). The adsorption kinetic models; Pseud first order, pseud second order, intra-particle diffusion and mass transfer models were used for analyzing the kinetic of maltose sorption by GAC. The findings indicates that maltose sorption onto GAC is well represented by the pseud second order model.

Keywords: GAC, MOD, Maltose, Kinetic

1. Introduction

Particularly reverse osmosis (RO) is currently one of the most cost effective and successful technologies membrane processes, for water reclamation and seawater desalination (Khawaji, et al, 2008; Reddy, Ghaffour, 2007). However, with the cost of energy increasing, further reduction in energy consumption is desirable. Recently, the forward osmosis (FO) process has been actively investigated by various researchers as an alternative membrane technology due to its low energy requirement and high recovery (McCutcheon, 2007). The FO process requires a reliable draw solution with a higher osmotic pressure compares to the feed solution. It utilizes an osmotic pressure gradient across a highly selective membrane; such that only water can permeate from the feed solution side through the membrane via osmosis to the draw solution side. Various draw solutions at high concentration can have exceedingly high osmotic pressure, which may potentially lead to a much higher water flux and recovery as compared to the more expensive RO which utilizes hydraulic pressure. Recently, the FO process has been developed for seawater desalination. McCutcheon et al. (2005) presented a novel ammonia–carbon dioxide FO process for seawater desalination (Elimelech, 2007). The FO process has also been developed by Holloway et al. (2006) for the concentration of anaerobic digester concentrate with much success. It is also currently being used as the first of the 2-step FO/RO process for landfill leachate treatment (Cath et al, 2006) and this has also been suggested for wastewater treatment (Cath et al, 2005). The FO process is also actively being used as a process for the direct osmotic concentration of liquid food (Barbe et al, 1998; Petrotos, Lazarides, 2001; Dova et al, 2007). Others suggested the application of the FO process in controlling drug release in the human body (Cath et al, 2007) and more recently, Tang and Ng (2008) proposed the use of the FO process in brine concentration for brine disposal, which is critical for inland desalination.

FO has been evaluated for seawater and brackish water desalination (Kravath, Davis, 1975; Moody, Kessler, 1976; Cath et al, 2006; McCutcheon et al, 2006), wastewater concentration and reclamation (Cath et al, 2005; Cath et al, 2007; Nicol, 2013; Sami et al, 2014), and food concentration (Hamed et al, 2006; Özkar, 2006). FO can also be employed in conjunction with biological processes for wastewater reuse in osmotic membrane bioreactors (OMBRs) (Abia et al, 2006; Belhachemi et al, 2009).

The main advantage of FO is that it operates at very low hydraulic pressure which has high rejection of a broad range of contaminants (Cath et al, 2006; Cath et al, 2005), and may have lower fouling propensity and/or fouling that is more reversible than in RO processes (Kravath, Davis, 1975; Moody, Kessler, 1976; Barbe et al, 1998; Petrotos, Lazarides, 2001; Cath et al,
One key component for successful development of FO technologies is the selection of an optimal draw solution. The main criterion is that the draw solution has a higher osmotic pressure than the feed solution to produce high water flux.

The Manipulated Osmosis Desalination Process (MOD) cycle is shown schematically in Fig.1 (Abia et al., 2006). The two systems are integrated by a recirculating osmotic agent (OA). One key property of the OA, also often referred to as a draw solution, is that it has a higher osmotic pressure than the feed water. In summary, a concentrated osmotic agent is used to draw fresh water from the feed water in the FO system. Hence, the osmotic agent becomes diluted. The diluted osmotic agent is then “regenerated” by the removal of this fresh water in the regeneration system (RO membrane). Combing the operation of these two systems is a key design and operating factor that is necessary for an easy and reliable operation of the MOD process.

Key benefits of the MOD process include: lower fouling propensity and consequently lower operating costs; lower energy consumption than conventional RO, particularly with difficult feed waters; reduced membrane whole life costs, as a result of fewer replacements; provision of a double membrane barrier between feed water and desalinated water; reduction in capex and opex due to the process’s inherent ability to significantly reduce problematic seawater contaminants, such as boron.

In addition the lower costs and easier fabrication, due to extensive use of low pressure (plastic) pipework and fittings, and membrane development will provide significant benefits in terms of reduced chemical consumption, plant footprint and energy (Belhachemi et al., 2009).

In the MOD process, at present, the regeneration system is also membrane based (Belhachemi et al., 2009). The membranes are commercially available semi-permeable membranes and, although this step does consume energy, by careful selection of the osmotic agent and the system operating conditions, this energy consumption is minimized.

The osmotic agent is based upon a low cost, non-toxic, low viscosity, water soluble and commodity chemical. For the MOD process, in particular, the components of the osmotic agent are suitable for use in drinking water facilities. As for conventional RO facilities, the performance of a particular plant is dependent on the feed water conditions. For example, in conditions of high TDS or lower temperature feed water, additional FO membrane area or a higher strength osmotic agent may be required. The ability to vary membrane performance, membrane area and...
osmotic agent strength permits a greater degree of flexibility in design.

Solute Exchange Technique (SET) is a new method proposed in the previous study (El Nemr et al., 2008), which inserted into an MOD system. SET has been used in conjunction with the Forward Osmosis process as shown in Fig.2. In the SET technique, the organic solutes such as glucose or maltose which are used as Osmotic Agents in the Forward Osmosis process can be removed by adsorbing onto GAC prior to the RO membrane in the MOD system. Saturated GAC with solutes is then regenerated using one of the common cost effective regeneration techniques. The desorbed solutes are retained at the RO unit rejection line (osmotic agent feed line). The main advantages of using the SET technique over the RO membrane are diluting the solute concentration prior to pumping to the RO membrane, thereby reducing the energy consumption of the process; avoiding fouling and scaling problems and thus an increase in the longevity of the membrane; increasing the process recovery and reducing costs.

In the previous study (El Nemr et al., 2008), the reliability of Solute Exchange technique (SET) for the application of the Manipulated Osmosis Desalination System (MOD) was examined. The reliability of this technique was investigated by examining adsorption capacity of specific organic compounds such as glucose and maltose onto commercial granular activated carbon (mesh 12-20) manufactured by Sigma Aldrich Company in the UK. Glucose and maltose could be used as Osmotic Agents in an MOD system as the previous study explained. The parameters affecting solute adsorption onto GAC are pH of the solution, initial solution concentration, shaking period and speed, sorbent dose and temperature are also investigated experimentally. Additionally, the adsorption equilibrium isotherm was tested using the common isotherm modules; Langmuir and Freundlich. GAC exhibited a capability to adsorb glucose and maltose from their aqueous solutions.

Also the glucose adsorption process was chemisorption and in an agreed well with the Freundlich isotherm model, while, the maltose adsorption process was a chemical and in agreed well with the Langmuir isotherm model. According to the findings, the SET is reliable to be used with an MOD system which leads mainly to reduce energy consumption and accordingly, a reduction in the cost of water produced, prediction of the rate limiting step is an important factor to be considered in the sorption process. Both kinetic and equilibrium isotherm studies help to identify the sorption process mechanism. Predicting the mechanism is required for design purposes. For solid liquid sorption processes, the solute transfer is usually characterized by either external mass transfer boundary layer diffusion or intraparticle diffusion or both. Generally, the sorption dynamics can be described by the following three consecutive steps (Hameed et al., 2006).

- Transportation of the solute from the bulk solution through the liquid film to the adsorbent exterior surface;
- Solute diffusion into the pore of the adsorbent except for a small quantity of sorption on the external surface: parallel to this is the intraparticle transport mechanism of the surface diffusion.
- Sorption of solute on the interior surface of the pores and capillary spaces of the adsorbent.

The last step is considered to be an equilibrium reaction of the three steps. The third step is assumed to be rapid and considered to be negligible. The overall rate of sorption will be controlled by the slowest step which would be either film diffusion or pore diffusion. Several kinetics models have been proposed to clarify the mechanism of a solute sorption from aqueous solution onto sorbent as shown below (Hameed et al., 2006).

1.1 The pseudo-first-order kinetic model of Lagergren

The Lagergren model for the sorption of liquid / solid system based on solid capacity can be expressed as follows (Hameed et al., 2006):

\[
\frac{dq}{dt} = K_l (q_e - q_t)
\]

(1-1)

Where

\( q_t \) : sorbed amount at time, t

\( q_e \) : sorbed amount at equilibrium

\( K_l \) : the rate constant of pseudo first order sorption process.

The integrated rate law, after applying the initial conditions of \( q_t = 0 \) at \( t = 0 \) is:

\[
\log(q_e - q_t) = \log(q_e) - \frac{K_l}{2.303}t
\]

(1-2)

Plot of \( \log(q_e - q_t) \) versus \( t \) should give a linear relation from which \( K_l \) and \( q_e \) can be determined from slope and intercept of plot respectively, a straight line for pseudo-first-order kinetics, which allows computation of the sorption rate constant (\( K_l \)). If the experimental results do not follow equations 1.1 and 1.2, they will differ in two important aspects:

1. \( K_l (q_e-q_t) \) is not representing the number of available sites
2. \( \log(q_t) \) is not equal to the intercept of the plot of \( \log(q_t-q_e) \) against \( t \) (Hameed et al., 2006).

1.2 Ho and McKay Equation (pseudo-second-order)

The pseudo-second-order chemisorption kinetics may be expressed as (Hameed et al., 2006; Özkaya, 2006; Abia et al., 2006; Belhachemi et al., 2009):

\[
\frac{dq}{dt} = k_2 (q_e - q_t)^2
\]

(1-3)
Where:
\(K_z\) is the rate constant of sorption, Separating the variables in Equation (1-3) gives:
\[
\frac{dq_r}{(q_r - q_t)^2} = k_z dt
\] (1-4)

Then, integrating the above equation for boundary conditions from \(t = 0\) to \(t = t\) and from \(q_t = 0\) to \(q_t = q_t\) gives:
\[
\frac{1}{(q_r - q_t)} = \frac{1}{q_r} + k_z t
\] (1-5)

By integrating rate law, for a pseudo second-order reaction Equation (1-5) can be rearranged to obtain:
\[
q_t = \frac{1}{k_z q_r + \frac{1}{q_r} t}
\] (1-6)

This has a linear form of:
\[
\frac{t}{q_t} = \frac{1}{k_z q_r^2} + \frac{1}{q_r} t
\] (1-7)

If the initial sorption rate is
\[
h = k_z q_r^2
\] (1-8)

Then equations (1-7) and (1-8) can be used to derive (or obtain):
\[
q_t = \frac{t}{h} + \frac{t}{q_r}
\] (1-9)

And
\[
\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_r} t
\] (1-10)

Plot of \((t/q_t)\) and \(t\) of equation should give a linear relationship, where \(q_r\) and \(k_z\) are determined from slope and intercept of plot respectively Hameed et al., 2006).

1.3 The intra-particle diffusion model

In order to gain an insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the kinetic experimental results were fitted to the Weber's intra-particle diffusion (El Nemr et al., 2008) model. The kinetic results were analyzed by the intra-particle diffusion model to elucidate the diffusion mechanism, which is expressed as:
\[
q_t = k_i d t^{1/2} + C
\] (1-11)

Where \(C\) is the intercept and \(k_i\) is the intra-particle diffusion rate constant (mg/g h\(^{1/2}\)), which can be evaluated from the slope of the linear plot of \(q_t\) versus \(t^{1/2}\) (El Nemr et al., 2008). The intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater contribution of the surface sorption in the rate controlling step. If the regression of \(q_t\) versus \(t^{1/2}\) is linear and passes through the origin, then intra-particle diffusion is the sole rate-limiting step. However, the linear plots at each concentration did not pass through the (Vadivelan et al., 2005) origin. This indicates that intra-particle diffusion was not the only rate controlling step.

1.4 The mass transfer model

The mass transfer model is expressed as bellow (Vadivelan et al., 2005; Qadeer, Akhtar, 2005; Hammed et al., 2008):
\[
C_0 - C = D \exp(K_i t)
\] (1-12)

Where:
\(C_0\) is the initial ion concentration (mg/l)
\(C\) is the ion concentration at time, \(t\)
\(t\) is the contact time (shaking time) min
\(D\) is the fitting parameter.
\(K_z\) is a constant which is the mass transfer adsorption coefficient.

A linearized form of equation is:
\[
\ln(C_0 - C) = \ln D + K_z t
\] (1-13)

If the sorption of an ion is depicted by the mass transfer model, then plotting \(\ln(C_0 - C)\) vs time (\(t\)) will give a linear relationship where \(\ln D\) (as a measure of the apparent distribution ratio of adsorbed ion between the bulk solution and the adsorbent surface) and \(K_z\) can be determined from the intercept and slope of the plot, respectively. Finally, Sami et al. (2014a); Sami et al., (2014b), have tested the kinetic adsorption of sucrose and glucose onto granular activated carbon mesh 12-20, as draw solutions in SET-MOD combined system. The findings in these studies gave an indication that the sucrose and glucose are in a good agreement with pseudo second order model. The main target of the current study was to describe the kinetic adsorption of maltose onto granular activated carbon mesh12-20, supplied by sigma Aldrich.

2. The experimental work

2.1 Equipment

A Four digits weight balance (Sartorius research type) was used in this investigation. For pH measurements, a pH- meter (Mettler-Toledo Company in UK) with standard electrode was used. All experiments were carried out using water- bath shaker (Mickle...
Laboratory Eng. Co England) with variable speed (shaking rate from 112 to 200 rpm) at temperature varied between 20-40°C. The concentrations of glucose and maltose were determined using an HPLC instrument (Varian 385-LC ELSD with Evaporative Light Scattering Detector Column and with mobile phase 80% acetonitrile, flow rate 3.0 ml/min).

2.2 Materials and reagents

Commercial granular activated carbon Darco with mesh (12-20) and D- (+) maltose monohydrate compound with good purity (≥99.5%) supplied by Sigma Aldrich Company in the UK were used. Also, to adjust the pH of solutions, analytical reagent grade of sodium hydroxide (Assay: 98.05 %) and laboratory reagent grade of hydrochloric acid solution (Assay: 35.38%) supplied by Fisher Scientific Co, UK were used. All solutions and reagents were prepared by dissolving the weighed amount of these chemicals in deionized water.

2.3 Methods & Procedures

In this study, three kinetic experiments set were carried out. In the first experiment set, GAC samples of 0.5g were shaken separately with 100ml of 6000 mg/l maltose concentration solution at different shaking speeds of 45,100 and 145rpm for 8 hr. This experiments set was performed at an ambient temperature with pH range of 7-8. In each experiment, within suggested intervals time during the 8 hr, one mixture was taken from the shaker the solution was then filtered using Whitman filter paper grade-1 and filtrate solution samples restored at 4°C prior to analysis. The same procedure carried out using 1 and 3 g GAC, respectively. The maltose concentrations in the filtered solutions were determined using HPLC equipment and all the results of this study are presented in Figs.3-17 and in Tables.1 and 2.

3. Results and discussion

It is clear from Figs.3,4, and 5, that at different shaking speeds, the adsorption rate of maltose onto GAC was rapid at the initial period of contact time for all GAC doses and then increased constantly with the contact time for 5 and 10 g/l GAC sample doses, while it increased slightly for the 30g/l GAC sample dose. Also, from these figures, it can be seen that the adsorption capacity decreased with an increase in GAC sample dose.

The Pseudo first order, pseudo second order, intra-particle diffusion and mass transfer kinetic models are employed in this work. The obtained parameters for all kinetic models are presented in Figs.6-17 and in Tables.1 and 2.

In most of the cases, the pseudo first order equation of Lagergren did not apply throughout the contact time and is generally applicable over the initial (20-30 min) sorption. As seen from Table.1, the correlation coefficient was much higher in the pseudo second order rate equation compared with other models. Also, from this table, it was observed that calculated equilibrium sorption capacity (qe) at different shaking speeds and GAC samples doses for all models are not close to the experimental values except for pseudo second order. This gives an indication that the pseudo second order model agreed well with experimental data values.

From Table.2 and from Figs10-12, it was observed that, generally, the intra-particle diffusion rate decreased with an increased in GAC doses at different shaking rate(45-145 rpm), while, it increased with increasing the shaking rate for all GAC sample doses. The intercept(c) values which represent the boundary layer effect is increased with increasing the shaking speed, for all GAC doses. These values also increased with GAC doses for 5 and 10 gml/l, however at 145 rpm they decreased with GAC sample dose increases. Also, the lines of plotting (qt) vs (t^{1/2}) for all GAC’s sample doses and shaking speeds used do not pass through the origin, giving an indication that intra-particle diffusion is not the only rate controlling step and some other mechanisms are also involved.

From Table 2, it can be seen that parameter factor (D) increased with an increased GAC sample dose and shaking speed, while the mass transfer adsorption coefficient (Kd) in general decreased with increased GAC sample doses and shaking time.
Table 1: Kinetic parameters for glucose adsorption at different AC sample doses and shaking speeds (rpm) when initial concentration solution is 6000 mg/l

<table>
<thead>
<tr>
<th>Model</th>
<th>rpm</th>
<th>45 rpm</th>
<th>101 rpm</th>
<th>145 rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Eq.</td>
<td>R²</td>
<td>Eq.</td>
</tr>
<tr>
<td>Pseudo 1st order</td>
<td>5</td>
<td>y = -0.0031x + 2.613</td>
<td>0.659</td>
<td>y = -0.0043x + 2.6122</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>y = -0.0028x + 1.9418</td>
<td>0.696</td>
<td>y = -0.0033x + 2.538</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>y = -0.0026x + 2.0507</td>
<td>0.65</td>
<td>y = -0.0012x + 1.4649</td>
</tr>
<tr>
<td>Pseudo 2nd order</td>
<td>5</td>
<td>y = 0.0026x + 2.0693</td>
<td>0.874</td>
<td>y = 0.0025x + 0.2259</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>y = 0.0048x + 0.9094</td>
<td>0.985</td>
<td>y = 0.0027x + 0.1773</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>y = 0.0066x + 0.4237</td>
<td>0.905</td>
<td>y = 0.0077x + 0.0376</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td>5</td>
<td>y = 11.684x + 67.502</td>
<td>0.876</td>
<td>y = 12.572x + 78.452</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>y = 3.114x + 136.76</td>
<td>0.788</td>
<td>y = 11.894x + 83.646</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>y = 3.2346x + 63.508</td>
<td>0.652</td>
<td>y = 1.9512x + 93.531</td>
</tr>
<tr>
<td>Mass transfer</td>
<td>5</td>
<td>y = 0.002x + 6.5237</td>
<td>0.959</td>
<td>y = 0.002x + 6.6259</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>y = 0.0007x + 7.3371</td>
<td>0.746</td>
<td>y = 0.002x + 7.3166</td>
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<tr>
<td></td>
<td>30</td>
<td>y = 0.0012x + 7.7884</td>
<td>0.799</td>
<td>y = 0.0006x + 0.0495</td>
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Table 2: Kinetic parameters of maltose adsorption onto GAC

<table>
<thead>
<tr>
<th>rpm</th>
<th>45 rpm</th>
<th>101 rpm</th>
<th>145 rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kₑ, qₑ</td>
<td>Kₑ, qₑ</td>
<td>Kₑ, qₑ</td>
</tr>
<tr>
<td>5</td>
<td>7.37x10⁻³</td>
<td>365</td>
<td>409.4</td>
</tr>
<tr>
<td>10</td>
<td>6.65x10⁻³</td>
<td>215</td>
<td>87.45</td>
</tr>
<tr>
<td>30</td>
<td>5.99x10⁻³</td>
<td>152</td>
<td>112.9</td>
</tr>
<tr>
<td></td>
<td>Kₑ, qₑ</td>
<td>Kₑ, qₑ</td>
<td>Kₑ, qₑ</td>
</tr>
<tr>
<td>5</td>
<td>2.51x10⁻³</td>
<td>365</td>
<td>496.4</td>
</tr>
<tr>
<td>10</td>
<td>2.44x10⁻³</td>
<td>215</td>
<td>208.3</td>
</tr>
<tr>
<td>30</td>
<td>1.03x10⁻²</td>
<td>152</td>
<td>151.5</td>
</tr>
</tbody>
</table>

Fig. 5: Adsorption capacity profile of maltose with time onto different GAC sample doses when initial concentration solution is 6000 mg/l and shaking speed 145 rpm

Fig. 6: Pseudo first order kinetic plot for maltose adsorption at different GAC sample doses when shaking speed 45 rpm and initial concentration solution is 6000 mg/l
Fig. Pseudo first order kinetic plot for maltose adsorption at different GAC sample doses when shaking speed 100 rpm and initial concentration solution is 6000mg/l

Fig.8 Pseudo first order kinetic plot for maltose adsorption at different GAC sample doses when shaking speed 145 rpm and initial concentration solution is 6000mg/l

Fig.9 Pseudo second order kinetic plot for maltose adsorption at different GAC sample doses when shaking speed 45 rpm and initial concentration solution is 6000mg/l

Fig.10 Pseudo second order kinetic plot for maltose adsorption at different GAC sample doses when shaking speed 100 rpm and initial concentration solution is 6000mg/l

Fig.11 Pseudo second order kinetic plot for maltose adsorption at different GAC sample doses when shaking speed 145 rpm and initial concentration solution is 6000mg/l

Fig.12 Intra particle kinetic plot for glucose adsorption at different GAC sample doses when shaking speed 45 rpm and initial concentration solution is 6000mg/l
Conclusions

The results of this work can be summarized as follows:

- At different shaking speeds, the adsorption rate of maltose onto GAC was found to be rapid at the initial period of contact time for all GAC doses and then increased constantly with contact time for 5 and 10 gm/l GAC sample doses, while it increased slightly for the 30gm/l GAC sample dose. Also, from these figures, it can be seen that the adsorption capacity decreased with an increase in GAC sample dose.

- The correlation coefficient values using the pseud second order rate equation are much higher compare with that in other kinetic models. Also, calculated equilibrium sorption capacity (qe) at different shaking speeds and GAC samples doses for all models are not close to the experimental values except for pseud second order.
• Thus the pseudo second order model agreed well with the experimental data values of the maltose adsorption process onto GAC.

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