Comparison The Kinetics of The Uptake of Sugars From The Draw Solution

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ABSTRACT

   The present work includes studying the kinetics of the adsorption of two sugars (maltose and glucose) on activated carbon (GAC) and comparison between them. These sugars are used as draw solution in the forward osmosis process in MOD-SET system (manipulated osmosis desalination system, MOD combined with solute exchange technique, SET). In this work, batch experiment in a stirred tank was carried out to study kinetics adsorption. The experiment was carried out using HPLC to determine the concentrations of sucrose and maltose before and after adsorption. The kinetic models used are pseudo-first order, pseudo-second order, intraparticle diffusion and mass transfer model. The findings indicates that sucrose and maltose sorption onto GAC are both well represented by the pseudo second order model.
Keywords: GAC, MOD, Maltose, Kinetic

مقارنة حركيات الامتزاز للسكريات من محلول التناضح

الخلاصة

يتضمن البحث حركية امنرار لنوعين من السكر (المالتوز والكلوكوز) باستخدام الكاربون المنشط والمقارتة بينهم. هذه السكريات تستخدم كمحلول سحب في عملية التناضح الامامي في منظومة MOD-SET(منظومة تحلية المياه بالتناضح مرنبطة مع تقنية ازالة المذاب مثل تقنية الامتزاز). حيث بستخدم محلول السحب لسحب الماء من المحلول الملحي. في هذا البحث تم استخدام التجارب الدفعية لدراسة حركية الامتزاز. استخدمت عدد من الموديلات الحركية مثل   موديل الدرجة الاولى الزائفة وموديل الدرجة الثانية الزائفة زمزديل الانتشار داخل الجسيمات وموديل انتقال الكتلة. النتائج العملية بينت تطابق مع موديل الدرجة الثانية الزائفة.

INTRODUCTION

Reverse osmosis (RO) is currently the most widely desalination technology [1,2]. However, RO is an energy-intensive process and required high cost because of high pressure required especially for sea desalination. In addition to that RO process produced a great amount of global warming. This high energy consumption combined with environmental problems is encouraging to develop an alternative technology which is environmentally friendly. 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 [3]. 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.

One of the most promising alternatives is the Manipulated Osmosis Desalination (MOD) process, developed at the Centre for Osmosis Research and Application (CORA) at the University of Surrey. The Manipulated Osmosis Desalination Process (MOD) cycle is shown schematically in Figure (1) [4].
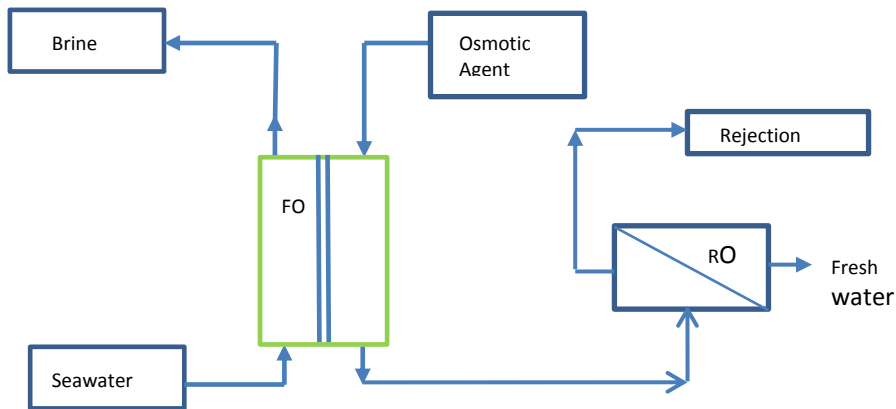

Figure (1): Schematic diagram of Manipulated Osmosis Desalination Process (MOD)

This process is based on membranes and consists of a Forward Osmosis system FO and a Reverse Osmosis RO or Nano filtration NF recovery step. The process exploits a particular draw solution which feeds both steps: the high osmotic pressure of the draw solution permits to extract the water from seawater or brackish water by a forward osmosis step, afterwards the diluted draw solution is re-concentrated in a Reverse Osmosis regeneration step and recycled to the first step. The whole process permits to product fresh water at lower energy consumption, as the pressure required for the reverse osmosis regeneration step is about 65 bars in place of 85 required for a traditional seawater reverse osmosis.

Solute Exchange Technique (SET) is a new method proposed in the previous study [5], which inserted into an MOD system. SET has been used in conjunction with the Forward Osmosis process as shown in Figure (2).
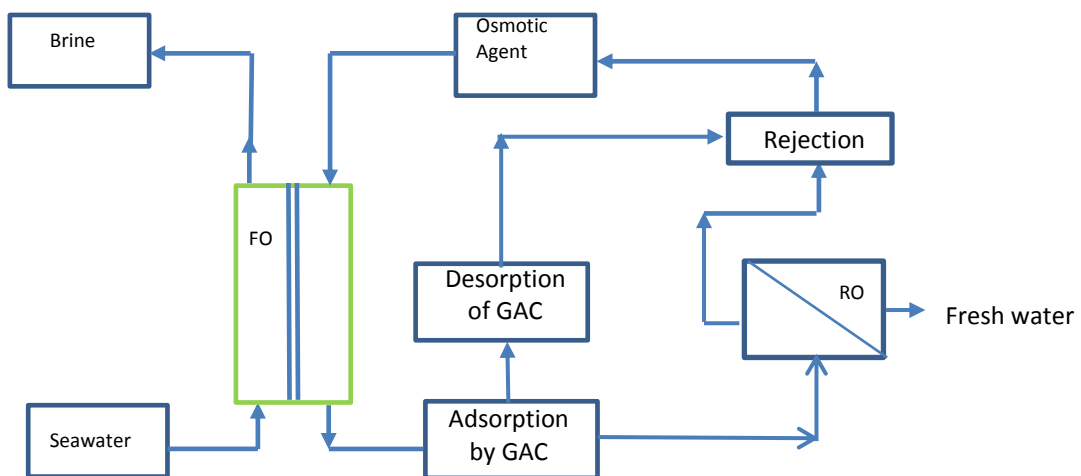
Figure (2): Schematic diagram of Solute Exchange Technique (SET) combined with MOD system

In the SET technique, the organic solutes such as maltose or glucose 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. SET technique including the adsorption process. So the present work aimed to study kinetics of GAC to remove of maltose and glucose from draw solution and comparison between them.

Kinetic Models

The prediction of kinetics is necessary for the design of adsorption systems. Several kinetics models have been proposed to clarify the mechanism of a solute sorption from aqueous solution onto sorbent as shown below:

Pseudo First Order Equation (Largergren Model)

The pseudo first-order equation [6] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_l(q_e - q_t) \qquad \ldots (1)$$

Where q_e and q_t are adsorption capacity at equilibrium and at time t and k_1 is the rate constant of pseudo first order adsorption process (min^{-1}). The integrated form of equation (1) after applying the boundary conditions $q_t = 0$ at t = 0 is:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_l}{2.303}t \qquad \ldots (2)$$

Plot of log (q_e-q_t) versus t should give a linear relation from which k_1 and q_e can be determined from slope and intercept of plot respectively.

The Pseudo Second- Order Equation

The pseudo second-order equation is generally expressed as follows [7]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad \ldots (3)$$

Where k_2 is the rate constant of pseudo second order adsorption (g/mg min). Integrating this for boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$ gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \qquad \ldots (4)$$

Equation (4) is the integrate rate law for a pseudo second-order- reaction. Equation (4) can be rearranged to obtain:

$$q_t = \frac{1}{(\frac{1}{k_2 q_e}) + (\frac{t}{q_e})} t \qquad \ldots (5)$$

This has a linear form of:

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e{}^2} + \frac{1}{q_e}t \qquad \ldots(6)$$

If the initial adsorption rate, h (mg/g min) is:

$$h = k_2 q_e{}^2 \qquad \ldots(7)$$

Then equations (6) and (7) become:

$$\left(\frac{t}{q_t}\right) = \frac{1}{h} + \frac{1}{q_e}t \qquad \ldots(8)$$

Plot of (t/q_t) and t of equation (8) should give a linear relationship, from which q_e and k_2, can be determined from slop and intercept of plot respectively.

The Elovich Equation

The Elovich model equation is generally expressed as [8,9]:

$$\frac{dq_t}{dt} = \alpha \exp\left(-\beta q_t\right) \qquad \ldots(9)$$

Chien and Clayton (1980) simplify the Elovich equation by assuming $\alpha\beta t >> t$ and by applying the boundary conditions $q_t = 0$ at t = 0 and $q_t = q_t$ at t = t, equation (9) becomes:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad \ldots(10)$$

Where β (g/mg) and α (mg/g/min) are the Elovich constants corresponding to the extent of surface coverage and rate of sorption at zero coverage respectively [10]. These constants were determined from the linear plot of q_t versus lnt where the slope of the line is (1/β) and the intercept is (1/β) ln($\alpha\beta$).

The Intraparticle Diffusion Model

The adsorption mechanism of a sorbate onto the adsorbent follows three steps: film diffusion, pore diffusion and intraparticle transport [11]. There is however, in the batch process the pore diffusion is the rate-limiting step and the sorption process is controlled by intraparticle diffusion [12, 13]. The Weber and Morris intra-particle diffusion model was then applied to analyze the kinetic data to explain the mechanism of diffusion as expressed in equation (11)

$$q_t = k_{id}t^{1/2} + C \qquad \ldots(11)$$

Where
C is the intercept and reflects the boundary layer effect. k_{id} is the intra-particle diffusion rate constant. These constants were determined from the plot of q_t vs $t^{1/2}$. The larger the intercept, the greater contribution of the surface sorption in the rate controlling step. If the regression of qt 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 origin [7, 8,14]. This indicates that the intra-particle diffusion was not only rate controlling step.

Material and Methods:

Material

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

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 (0-200 rpm) at temperature varied between 20-40°C. The concentrations of maltose and sucrose 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).

Kinetics Experiments

The kinetic study was carried out by batch experiments. The batch experiments were carried out at the room temperature of about 25°C by putting 50 ml of sugar solution of known concentration of 6000 mg/l in conical flask of 250 ml containing a required weight of GAC of 5, 10, and 30 g/l. The mixture was shaken by a machine of shaker at different time 0-8 hr. to reach equilibrium. Then, the solution filtered and analyzed using high performance liquid chromatography (HPLC). The amount of sugar adsorbed at time t, q_t (mg/g), was calculated by the following mass balance relationship:

$$q_t = \frac{V}{M}(C_O - C_t) \qquad \ldots (12)$$

Where:

C_o, and C_t are the sugar (Glucose or maltose) concentrations in mg/l initially and at a given time t, respectively,

V is the volume of the sugar solutions in ml

M is the weight of activated carbon in g.

The percentage removal of sugar (R %) is given by:

$$q_t = \frac{C_O - C_t}{C_t} \times 100 \qquad \ldots (13)$$

The pH of the solution in all experiments was adjusted to 8 by using 0.1N HCl and 0.1N NaOH.

Result and Discussion:
Effect of GAC Dosage

The effect of varying GAC dose (5, 10, and 30 mg/l) at different contact time for fixed volume (50 ml) of sugar solution (maltose and glucose) at constant concentration (6000 mg/l), is shown in Figures (3) and (4) for maltose and glucose respectively.
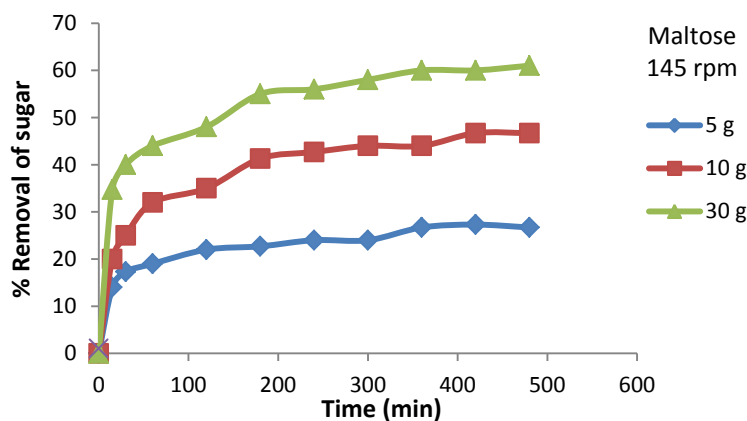
Figure (3): Influence of adsorbent dose on the adsorption of maltose (T=20 ^{o}C, pH = 8, initial glucose concentration is 6000 mg/l, shaking speed 145rpm.
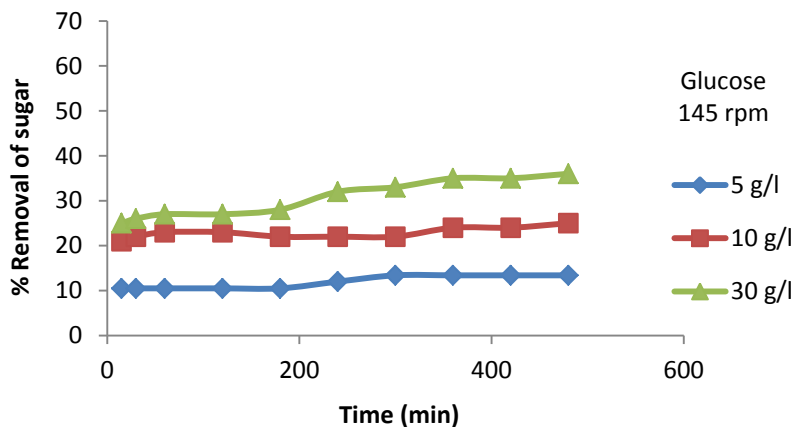

Figure (4): Influence of adsorbent dose on the adsorption of glucose (T=20 ^{o}C, pH = 8, initial glucose concentration is 6000 mg/l, shaking speed 145rpm.

   It is observed from these figures that increasing in GAC dose, increased in the percentage of sugar removal from aqueous solution. This results is expected because that by increasing in the dose of the GAC, the number of adsorption sites available for adsorption is increased, and the resulting in the increased in the percentage removal of sugar from solution [15].
It is clear from Figure (5) that the percentage removal of maltose is greater than glucose at the same condition. We conclude from these results that 30 g/l is the best dose of GAC that gives better percentage removal.
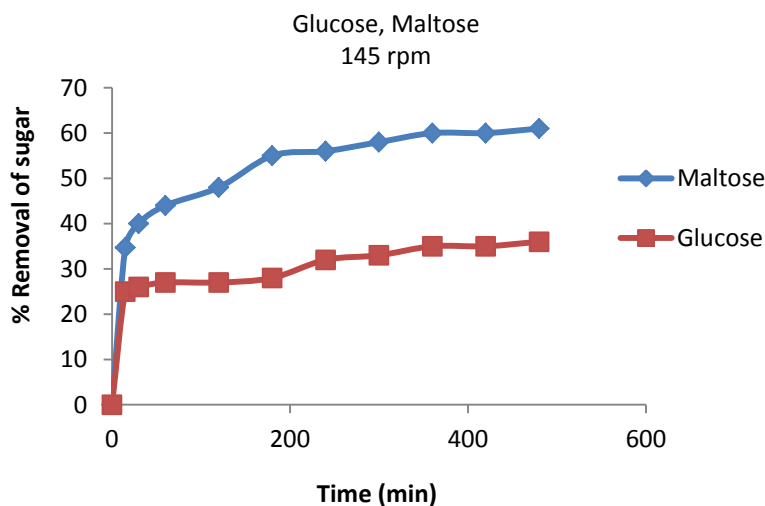

Figure (5): comparison the adsorption of maltose and glucose on GAC, (T=20 ^{o}C, pH = 8, initial concentration of maltose and glucose is 6000 mg/l, GAC dose 30 g/l, shaking speed 145 rpm).

Effect of Contact Time and Agitation Speed

The adsorption of sugar on GAC was studied at different agitation speed and at varying contact time (45, 100, and 145 rpm) as shown in Figures (6) and (7). It is clear from these figures that the percent removal increased with increasing in contact time and agitation speed. The maximum percent removal at the studied condition is 60 % for maltose and 40% for glucose at contact time 240 min and agitation speed of 145 rpm. It can be conducted from these results that the best conditions under studied state are 240 min contact time and 145 rpm agitation speed.
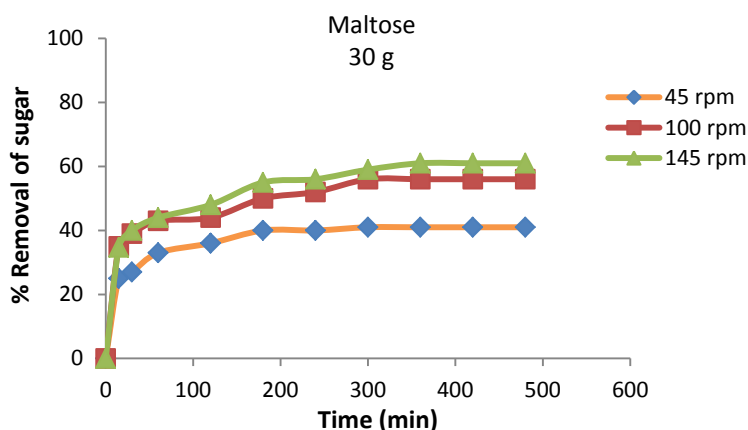

Figure (6): Influence of contact time and agitation speed on the adsorption of maltose
(T=20°C, pH = 8, initial glucose concentration is 6000 mg/l, GAC dose 30 g/l.
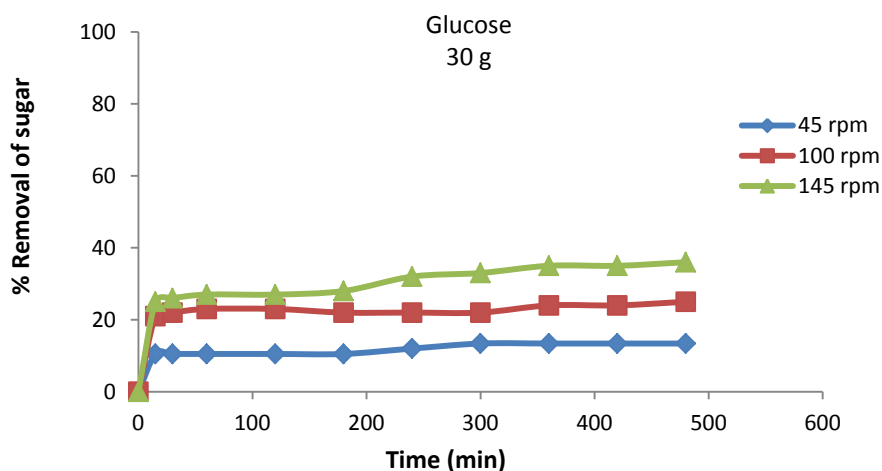

Figure (7): Influence of contact time and agitation speed on the adsorption of glucose
(T=20°C, pH = 8, initial glucose concentration is 6000 mg/l, GAC dose 30 g/l.

Kinetics Studies

The effect of contact time on adsorption kinetics for maltose and glucose adsorbed on GAC had been studied with initial concentration of 6000 mg/L at 20°C and pH 8.0 and at best condition of 30 g/l GAC dose, 240 min contact time and 145 rpm. Four adsorption kinetics modeled are employed in the present work. These models are: pseudo first-order Lagergren, pseudo second-order rate equation, and Elovich and intra-particle diffusion equations. Linear plots of all considered kinetic models are shown in Figures (8 – 11). The parameters for all

kinetics model and the correlation coefficients are presented in Table (1) for maltose and glucose.

Figure (8) shows the applicable of pseudo first-order to experimental data of both maltose and glucose. Although the plot is a straight line, the experimental q_e value does not agree with the calculated once that obtained from the linear plots of log (q_e-q_t) versus t. Also the regression values R^2 was 0.6587 and 0.7902 for maltose and glucose respectively. These values of q_e and the regression R^2 (Table (1)) indicate that the sorption data fitted poor to pseudo first order kinetics. Hence the adsorption of sugar (maltose and glucose) onto GAC may be not following the pseudo first order expression.
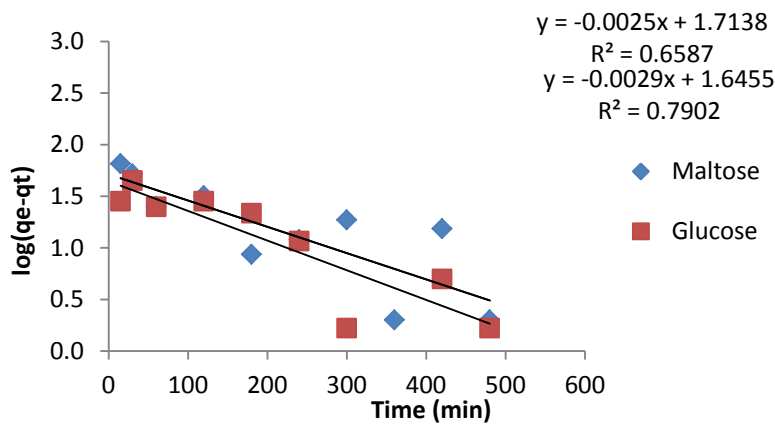

Figure (8): Pseudo first-order kinetic plot for the adsorption of maltose and Glucose on GAC

The pseudo second-order kinetic model (equation (6)) was applied to the experimental data of adsorption of maltose and glucose on GAC as shown in Figure (9). As shown in Figure (9) the plot of t/q_e against t for both sugars is a straight line. The parameters q_e and k_2 can be determined from the slope and intercept of the linear plot. The linear plot of t/q_e against t shows a good agreement between the experimental and calculated value of q_e as shown in Table (1).
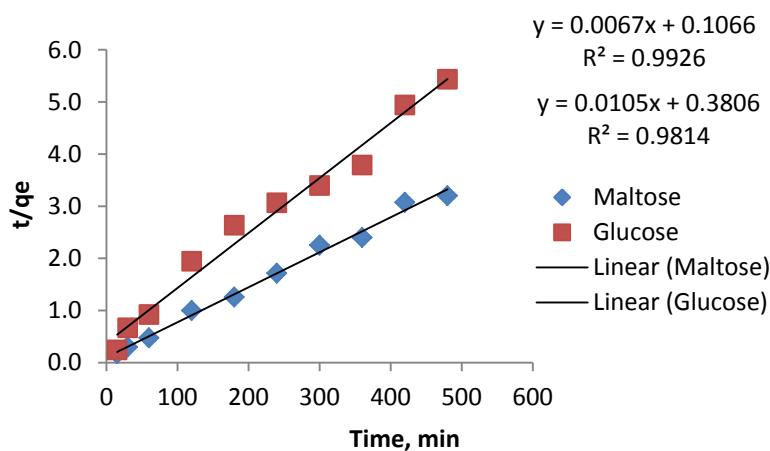

Figure (9): Pseudo second-order kinetic plot for the adsorption of maltose and Glucose on GAC

The correlation coefficient R^2 for the pseudo second-order model of maltose and glucose are 0.9926 and 0.9814 respectively. These values of R^2 and q_e illustrated in Table (1) indicating that the pseudo second order kinetics describes the adsorption of maltose and glucose by GAC much better than pseudo first order model. It could be concluded that the mechanism of adsorption was pseudo-second order reaction. This conclusion is agreement with those studies that have proven that the pseudo second-order kinetic model is reasonably good fit of data over the entire adsorption process [16-19].

Figure (10) shows the applied Elovich kinetic model (equation (10)) for the adsorption of maltose and glucose onto GAC.
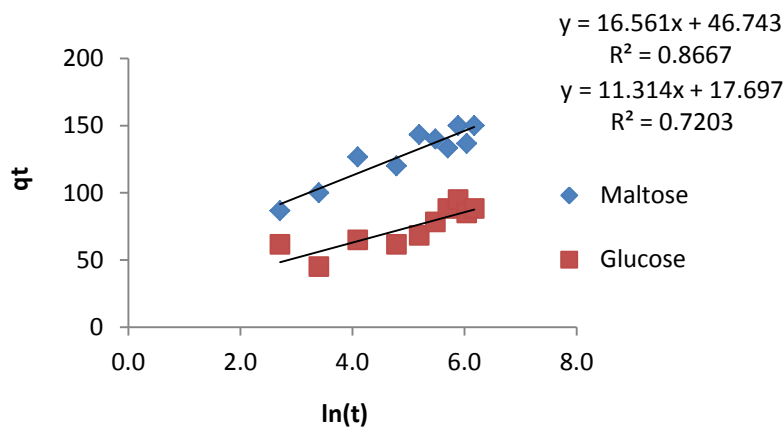

Figure (10): Elovich kinetic plot for the adsorption of maltose and Glucose on GAC

The Elovich parameters β and α were determined from the linear plot of q_t against ln(t) as shown in Figure (10) and the regression value R^2 are presented in Table 1. The value of R^2 for maltose and glucose is 0.8667 and 0.7203 respectively. These values of R^2 indicate that the adsorption data fitted poor to the Elovich kinetic model.
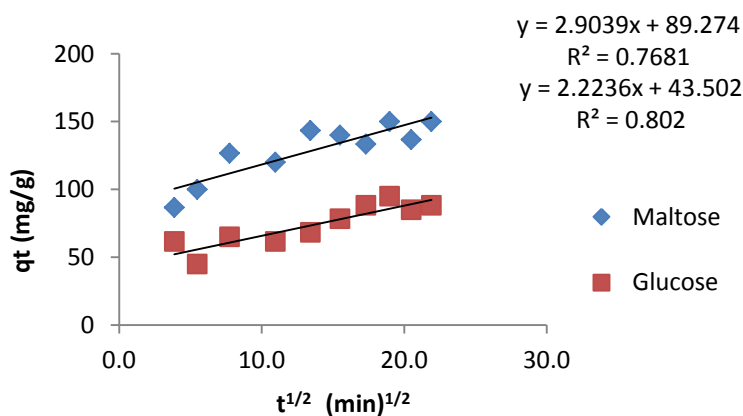

Figure (11): Intra-particle diffusion model plot for the adsorption of maltose and Glucose on GAC

Table (1). Kinetic parameters for the adsorption of Sugar onto GAC.

Models	Maltose			Glucose		
	Coefficients	R^2		Coefficients	R^2	
Pseudo-first order	$k_1 = 5.76 \times 10^{-3}$ min^{-1} q_e (exp) = 152 mg/g q_e (cal) = 52 mg/g	0.6587		$k_1 = 6.68 \times 10^{-5}$ min^{-1} q_e (exp) = 90 mg/g q_e (cal) = 49 mg/g	0.7902	
Pseudo-second order	$k_2 = 4.22 \times 10^{-4}$ g/mg min q_e (exp) = 152 mg/g q_e (cal) = 149 mg/g	0.9920		$k_2 = 2.9 \times 10^{-4}$ g/mg min q_e (exp) = 90 mg/g q_e (cal) = 95 mg/g	0.9814	
Elovich equation	$\beta = 0.06$ $\alpha = 280$	0.8667		$\beta = 0.06$ $\alpha = 48$	0.7203	
Intra-particle diffusion	$k_{id} = 3.90$ $C = 89$	0.7681		$k_{id} = 2.22$ $C = 44$	0.8020	

The intra-particle diffusion model is the most model used to describe the mechanism of adsorption process. This model (equation (11)) was applied to the experimental data as shown in Figure (11). A plot of qt versus t$^{1/2}$ should give a straight line and the model parameters k$_{id}$ and C were determined from the slop and the intercept. These model parameters are presented in Table (1). The intra-particle diffusion is the only rate limiting controlling the adsorption process if the plot of q$_t$ versus t$^{1/2}$ is a straight line passes through origin. Otherwise if the plot deviates from the origin then some other mechanism along with the inter-particle is also involved. The linear plot for maltose and glucose did not pass through the origin. This deviation from origin means that the rate limiting step was not only intra-particle diffusion but also other surface phenomena on the adsorption process. The values of the correlation coefficient R^2 values for maltose and glucose are 0.7681 and 0.8020 respectively. The values of R^2 indicated poor fitting of the experimental data to the intra-particle diffusion model. This means that the external mass transfer is the main rate controlling step in the adsorption process of maltose and glucose onto GAC.

CONCLUSION
The results of this work can be summarized as follows:
- The best condition for the removal of maltose and glucose by GAC for the present work is: 30g/l GAC dosage, 240 min contact time, and 245 rpm agitation speed
- The ability of GAC to remove maltose (60 %) is greater than for glucose (40 %).
- The correlation coefficient values using the pseudo second order rate equation are much higher compare with that in other kinetic models. Also, calculated equilibrium adsorption capacity (q$_e$) for maltose and glucose for all models is not close to the experimental values except for pseudo second order. Thus the pseudo second order model agreed well with the experimental data values of the maltose and glucose adsorption process onto GAC.

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