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Saving amberlite XAD4 by using inert material in adsorption process

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ABSTRACT

The effect of partially replacing amberlite XA4 in fixed adsorbent beds by inert materials (glass beads) in an adsorption process of methylene blue onto amberlite XAD4 was investigated. Experiments were carried out to study the effect of various amberlite XAD4-glass beads weight ratios, influent methylene blue concentrations, flow rate and bed depth on the performance of fixed bed. The equilibrium data were fitted with theoretical models using interparticle diffusion coefficients obtained from separate batch adsorber experiments. Results suggest that replacing 5% by weight amberlite XAD4 by glass beads increasing the breakthrough time of the adsorbent bed by 80%. While adding 7% glass beads reduce the weight of amberlite XAD4 by 7% and increase the breakthrough time by 20%. However, replacing 10% of amberlite XAD4 makes the adsorption process inefficient compared with 0% glass beads. A mathematical model was formulated to describe the mass transfer kinetics in the fixed bed adsorber. The results show that the mathematical model includes external mass transfer and pore diffusion using nonlinear isotherms, provides a good description of the adsorption process for methylene blue onto fixed bed adsorber.

Keywords: Adsorption; Fixed bed; Amberlite XAD4; Methylene blue; Glass beads; Mathematical model; Mass transfer coefficient.

1. Introduction

Methylene blue (MB), a cationic dye, is not regarded as astutely toxic, but it has various harmful effects. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting and gastritis problems [1,2].

MB is slightly hazardous in the case of skin contact (irritant), of eye contact (irritant), and of ingestion and inhalation, mutagenic for mammalian somatic cells and bacteria and/or yeast. Repeated or prolonged exposure is not known to aggravate medical condition [3].

The polymer XAD4 is rigid, non-ionic, crosslinked macrorecticular copolymer of styrene and divinylbenzene, with high surface area and, aromatic nature of its surface and supplied as white insoluble beads. Amberlite XAD4 is a polymeric adsorbent with excellent physical, chemical, and thermal stability and it is also stable at all pH range in aqueous solution, its characteristic pore size distribution make this Amberlite an excellent adsorbent of organic substances [4].

Amberlite XAD4 polymeric adsorbent can be used through repeated cycles, in column or batch modes, to adsorb hydrophobic molecules from polar solvents or volatile organic compounds from vapor streams. Its characteristic pore size distribution makes Amberlite XAD4 an excellent choice for the adsorption of organic substances of relatively low molecular weight [5,6].

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To design and operate a fixed bed adsorption process successfully, the column dynamics must be understood; that is the breakthrough curves under specific operating conditions must be predictable. A mathematical model of fixed bed adsorber is very useful for the proper design and the determination of the optimal operating conditions. Different models for the adsorption process on fixed beds were proposed in the literature [7] and various numerical techniques have been developed for the solution of these models. The differences between these models arise from the different representation of the equilibrium behavior, the different expressions of the mass transfer inside and outside the adsorbent particle and from how the axial dispersion is taken into account in the material balance for the adsorbate in the fixed bed column.

Several rate models have been developed that take into account an external film transfer rate step, unsteady state transport in the solid phase and nonlinear equilibrium isotherm to predict adsorption rates in batch reactor and fixed bed [8].

Under a wide range of operating conditions, the key process parameters in adsorption such as isotherm constants and mass transfer coefficients are obtained by conducting batch studies of adsorption. Langmuir, Freundlich, Radke–Prausnitz, Reddlich–Peterson and combination of Langmuir–Freundlich isotherms have been applied to describe the equilibrium between liquid–solid phases. The parameters that are responsible for mass transfer operation are the external mass transfer coefficient and interparticle diffusivity or surface diffusion coefficient.

The liquid hold-up is an important characteristic of packing owing to its relation to the wetted area. There are two types of hold-up; static and dynamic (operating) hold-up. The static hold-up was measured as the weight of liquid retained when the column has drained to a constant weight; this was deducted from the total hold-up to obtain the operating hold-up [9]. Investigators measured the hold-up for different aqueous solutions and they found that the static hold-up for carbon is greater than that for porcelain, which may be due to porosity of carbon material [9]. Experimental work showed that for water flowing over vertical column of spheres, the total hold-up was equal ($0.4 + 0.596\ l^{1/3}$) g per sphere, where l is the flow rate, cm^3/s [10]. The first term is the static hold-up due to the meniscus at the junction of the spheres and the second term is the dynamic hold-up in the liquid film. Other investigators found that the dynamic hold-up on random packing varied as a power of the liquid rate between 0.54 and 0.74 [11,12]; this difference between this power and the theoretical value of 0.33 can be attributed to changes in the wetted area of the packing.

The objective of this study is to investigate the effect of partially replacing Amberlite XAD4 with inert material, such as glass beads on the removal of methylene blue by adsorption using Amberlite XAD4. The ultimate aim is to prove that the system can be made more efficient and /or economical by increasing the adsorption surface area of the adsorbent through the reduction of dead zones between the particles in a fixed bed. To achieve this objective an experimental programme was designed and performed using different Amberlite XAD4-glass beads ratios, methylene blue concentrations, flow rate and bed depth. The experimental results were compared with that obtained by theoretical formulation of the general rate model which includes axial dispersion, film mass transfer, pore diffusion resistance and nonlinear isotherm.

2. Theory

2.1. Fixed bed

Fixed bed dynamics are described by the convection-diffusion equations, coupled with source term due to adsorption and diffusion inside adsorbent particles. The solution of these equations will give rise to the prediction of the needed breakthrough curves [13].

General rate model refer to models containing a rate expression, or rate equation, which describe the interfacial mass transfer between the mobile phase and the stationary phase. A general rate model usually consists of two sets of differential equations, one for the bulk phase, and the other for the particle phase [14].

The rate model considers the following; axial dispersion, external mass transfer, interparticle diffusion and nonlinear isotherm [15,16].

For modeling of fixed bed adsorption the column is divided into the bulk-fluid phase and the particle phase. The model equations are based on the hypothesis of an interparticle mass transfer controlled by diffusion into macropores (pore diffusion model), and this approach considers three phases; they are: the mobile phase in the space between particles, the stagnant film of mobile phase immobilized in the macropores and the stationary phase where adsorption occurs [17,18].

The following basic assumptions are made in order to formulate the model [13]:

- Adsorption process is isothermal.
- The packing material is porous, spherical, particles of uniform size.
- The concentration gradient in the radial direction of the bed is negligible.
- Local equilibrium exists for the component between the pore surface and the stagnant fluid phase in the pores.
- The film mass transfer mechanism can be used to describe the interfacial mass transfer between the bulk-fluid and particle phase.
- The dispersion coefficient is constant.
- Surface diffusion can be ignored.

Continuity equation of the mobile phase is:

$$-D_b \frac{\partial^2 C_b}{\partial Z^2} + \nu \frac{\partial C_b}{\partial Z} + \frac{\partial C_b}{\partial t} + \rho_p \frac{1-\varepsilon_b}{\varepsilon_b} \frac{\partial q}{\partial t} = 0 \tag{1}$$

Using C_p, the concentration in the stagnant mobile phase and writing the expression of the interfacial flux leads to [14]:

$$\rho_p \frac{\partial q}{\partial t} = \frac{3k_f}{R_p}\left(C_b - C_{p,R=R_p}\right) \tag{2}$$

Substituting Eq. (2) in Eq. (1) gives:

$$-D_b \frac{\partial^2 C_b}{\partial Z^2} + \nu \frac{\partial C_b}{\partial Z} + \frac{\partial C_b}{\partial t} + \frac{3k_f\left(1-\varepsilon_b\right)}{\varepsilon_b R_p}\left[C_b - C_{p,R=R_p}\right] = 0 \tag{3}$$

The particle phase continuity equation in spherical coordinates is:

$$\left(1-\varepsilon_p\right)\frac{\partial C_p^*}{\partial t} + \varepsilon_p \frac{\partial C_p}{\partial t} - \varepsilon_p D_p \left[\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2 \frac{\partial C_p}{\partial R}\right)\right] = 0 \tag{4}$$

Defining the following dimensionless formula [14]:

$$c_b = \frac{C_b}{C_o}, \quad c_p = \frac{C_p}{C_o}, \quad c_p^* = \frac{C_p^*}{C_o}, \quad \tau = \frac{\nu t}{L}, \quad r = \frac{R}{R_p}, \quad z = \frac{Z}{L},$$

$$Pe_L = \frac{\nu L}{D_b}, \quad Bi = \frac{k_f R_p}{\varepsilon_p D_p}, \quad \eta = \frac{\varepsilon_p D_p L}{R_p^2 \nu}, \quad \zeta = \frac{3Bi\eta\left(1-\varepsilon_b\right)}{\varepsilon_b}.$$

The model equations can be transformed into the following dimensionless equations:

$$-\frac{1}{Pe_L}\frac{\partial^2 c_b}{\partial z^2} + \frac{\partial c_b}{\partial z} + \frac{\partial c_b}{\partial \tau} + \zeta\left(c_b - c_{p,r=1}\right) = 0 \tag{5}$$

$$\frac{\partial}{\partial \tau}\left[\left(1-\varepsilon_p\right)c_p^* + \varepsilon_p c_p\right] - \eta\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c_p}{\partial r}\right)\right] = 0 \tag{6}$$

The concentration c_p^* in Eq. (6) is the dimensionless concentration in the solid phase of the particles. It is directly linked to the isotherm, which is the extended Langmuir model:

$$C_p^* = \frac{q_m b \rho_p C_p}{1 + bC_p} \tag{7}$$

The concentration c_p^* in dimensionless form:

$$c_p^* = \frac{\rho_p q_m b c_p}{1 + bC_o c_p} \tag{8}$$

Finite element method is used for discretization of the bulk-fluid phase partial differential equation and the orthogonal collocation method for the particle phase equation, an ordinary differential equation system is produced. The ordinary differential equation system with initial values can be readily solved using an ordinary differential equation solver such as the subroutine “ODE15S” of MATLAP which is a variable order solver based on the numerical differentiation formulas (NDFs). Optionally it uses the backward differentiation formulas (BDFs), which is also known as Gear's method.

2.2. Batch adsorber

The batch model is the following:

- Mass balance in the bulk-fluid phase

$$V_L \frac{dC_b}{dt} + \frac{3W_A}{\rho_p R_p} k_f \left(C_b - C_{p,r=R_p}\right) = 0 \tag{9}$$

where V_L = volume of fluid in the batch adsorber; W_A = mass of activated carbon in the batch adsorber.

- Mass balance inside the particle

The solute diffusion inside a spherical particle is described by the following equation:

$$\varepsilon_p \frac{\partial C_p}{\partial t} + \rho_p \frac{dq}{dt} = \varepsilon_p D_p \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_p}{\partial r}\right) \tag{10}$$

The solute concentration in the pores is in local equilibrium with the concentration of solute adsorbed on the pore walls.

For Langmuir isotherm model:

$$q = \frac{q_m b C_p}{1 + bC_p} \tag{11}$$

The external mass transfer coefficient for the solute adsorbed at certain particle size and optimum speed, can be obtained by the analytical solution (19,20).

$$k_f = -\frac{R_p \rho_p V_L}{3W_A t}\ln\left(\frac{C_t}{C_o}\right) \tag{12}$$

where R_p and ρ_p are the particle radius and density respectively and C_o and C_t are the solute concentration at time zero and time t, respectively.

Experimental concentration-time data are compared to predicted concentration-time profile for the above batch absorber model and the best statistical description used to determine the interparticle pore diffusion coefficient.

3. Experimental work

3.1. Materials

Adsorbate: methylene blue dye was used as pollutant; it was supplied by Sigma-Aldrich Company Ltd., UK.

Adsorbent: Amberlite XAD4 was used as an adsorbent; it was supplied by Sigma-Aldrich Company Ltd., UK.

Inert materials: glass beads were supplied by Sigma-Aldrich Company Ltd., UK.

3.2. Methods

The Amberlite was sieved on 28/32 mesh with geometric mean diameter of 0.5 mm. For pre-treatment, the resin was washed with distilled water then cleaned by extraction using methanol as a solvent, for the removal of residual monomer, after that all particles were washed with distilled water then dried at 100°C for 24 h before being used as adsorbent. The aqueous solution of methylene blue was prepared using reagent grades. The glass beads were sieved on 28/32 mesh with geometric mean diameter of 0.5 mm. The glass beads were washed and dried at 100°C for 24 h.

The fixed bed experiments were carried out in acrylic column of 30 cm height, 7.5 cm internal diameter. The Amberlite bed was supported in the column by a fine porous stone; the influent solution was introduced to the column through a perforated plate, fixed at the top of the column. Feed solution was prepared in polyethylene square tank. A schematic diagram of the apparatus is shown in Fig. 1. The system temperature was 20°C.

For the determination of adsorption isotherms, 250 ml flasks were filled with known concentration of solute and a known weight of Amberlite XAD4. The flasks were then placed on a shaker and agitated continuously for 5 days at 20°C. The concentration of methylene blue in the solution was determined by GC device (type Perkin Elmer Clarus MS500).

The adsorbed amount is calculated by the following equation:

$$q_e = \frac{V_L\left(C_o - C_e\right)}{W_A} \tag{13}$$

The interparticle diffusion coefficient was estimated using the following steps:

- Estimating the optimum agitating speed for batch adsorber to reach the needed equilibrium concentration of MB.
- Estimating the mass transfer coefficient in batch process at optimum agitation speed.
- Apply numerical solution of batch adsorber model to obtain the interparticle diffusion coefficient. This was done by using the pore diffusion model to best fit the experimental results.

The interparticle diffusion coefficient for methylene blue was obtained by using 2 L Pyrex beaker fitted with a variable speed mixer. The beaker was filled with 1 L of known concentration solution and agitation started before adding the Amberlite XAD4. At time zero, the accurate weight of Amberlite XAD4 was added. Samples were taken every 15 min.

Different agitation speeds of 700, 800, 900, 1000 and 1100 were carried out to achieve $C_e/C_o = 0.05$.

The interparticle pore diffusion coefficient was derived from the typical concentration decay curve for the solute at optimum agitation speed and dosage of Amberlite by an iterative search technique predicted on the minimization of the difference between experimental and predicted data from pore diffusion model.

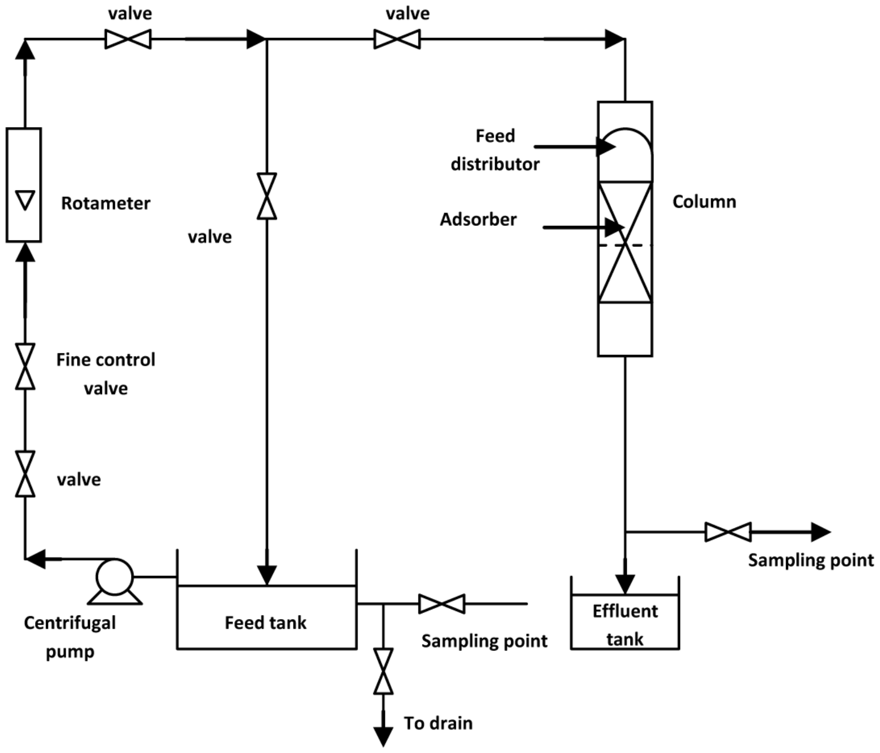

Fig. 1. Schematic representation of experimental equipment.

The necessary dosage of Amberlite XAD4, to reach equilibrium related concentration of C_e/C_o equal 0.05, were calculated from isotherms model and mass balance equation.

Bed porosity measurements for different glass beads-Amberlite weight ratios were done by using a volumetric container. Different mixtures were prepared; the container was filled with different mixture at a time and weighted. Distilled water was added to the edge of the mixture and weighted; the bed porosity was calculated by dividing the void volume by the volume of the container.

4. Results and discussion

4.1. Adsorption isotherm

The adsorption isotherms display a nonlinear dependence on the equilibrium concentration. The adsorption data for the system was fitted by Langmuir [21], Freundlich [22], Radke-Prausnitz [23], Reddlich–Peterson [24] and combination of Langmuir–Freundlich isotherm [25] isotherm models. The determination coefficients are shown in Table 1. Table 1 indicates that the Langmuir model provides the best fit as judged by its correlation coefficient. The Langmuir model was therefore selected to be introduced in the fixed bed model:

Table 1
Parameters of isotherm for MB and correlation coefficient for various models

Model	Parameters	Methylene Blue
Langmuir $q_e = \frac{q_m b C_e}{1 + bC_e}$	q_m, b, l/mg Correlation coefficient	8.0 4.3 0.9898
Freundlich $q_e = KC_e^{1/n}$	K, n, Correlation coefficient	8.1419 1.2163 0.9514
Radke–Prausnitz $q_e = \frac{K_{RP} C_e}{1 + \left(\frac{K_{RP}}{F_{RP}}\right) C_e^{1-N_{RP}}}$	K_{RP}, F_{RP}, N_{RP}, Correlation coefficient	7.0905 8.0988 –0.7726 0.9711
Reddlich–Peterson $q = \frac{A_R C_e}{1 + B_R C_e^{m_R}}$	A_R, B_R, m_R, Correlation coefficient	1.1027 0.0793 1.0995 0.5689
Combination of Langmuir–Freundlich $q_e = \frac{b q_m C_e^{1/n}}{1 + bC_e^{1/n}}$	q_m, b, n, Correlation coefficient	9.5871 4.8389 46.4876 0.9855

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{14}$$

The equilibrium isotherms for methylene blue onto Amberlite XAD4 is presented in Fig. 2.

4.2. Interparticle diffusion coefficient

The amounts of Amberlite XAD4 used for adsorption methylene blue was calculated for final equilibrium related concentration of $C_e/C_o = 0.05$. The Langmuir model constants were used with the mass balance in 1 L of solution. The initial concentrations were 0.2 kg/m^3 with the doses of Amberlite XAD4 of 24×10^{-3} kg.

The typical concentration decay curves of solute in batch experiments were carried out for methylene blue at different agitation speeds as shown in Fig. 3. The optimum agitation speed needed to achieve $C_e/C_o = 0.05$ was found to be 1000 rpm. It is clear that if the speed is above 1000 rpm, the equilibrium relative concentration is less than 0.05; this is due to pulverization of Amberlite XAD4 at high speed agitation.

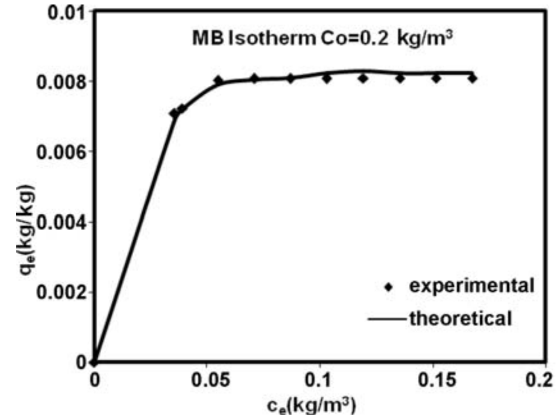

Fig. 2. Adsorption isotherm for MB onto Amberlite XAD4 at 293K.

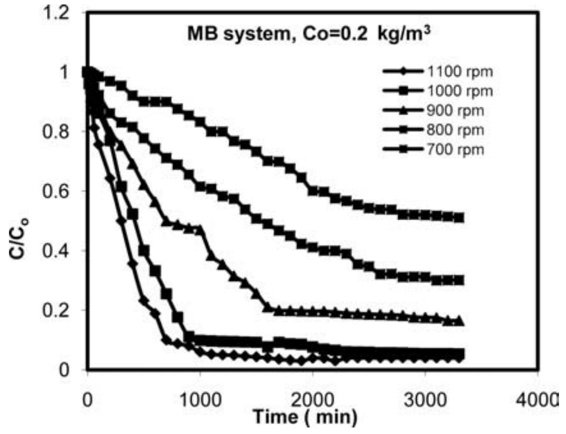

Fig. 3. Concentration–time decay curves for MB adsorption onto Amberlite XAD4 at different agitation speeds.

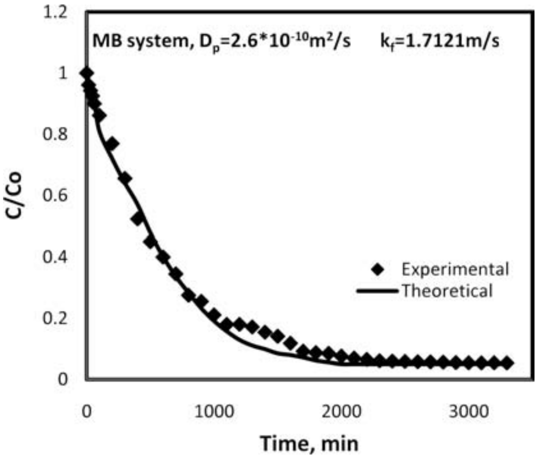

Fig. 4. Comparison of the measured concentration-time data with that predicted by pore diffusion model in batch adsorber for MB system.

The pulverization of Amberlite appeared on the filter paper when the slurry of Amberlite was filtered after agitation above 1000 rpm. Drying and sieving the pulverized particles were done and the particles size was reduced.

There was a good matching between batch experimental results and predicted data using the pore diffusion model for batch operation as shown in Fig. 4.

The pore diffusion coefficient for the system is evaluated from the batch experiment to be $D_p = 2.6\times10^{-10}$ m^2/s.

The external mass transfer coefficients in packed bed model for the system were evaluated by using the correlation of Wilson and Geankoplis [26].

$$\text{Sh} = \frac{1.09}{\varepsilon_b}\text{Sc}^{1/3}\,\text{Re}^{1/3} \quad \text{for Re} = 0.0915-55 \tag{15}$$

where Sh = $K_f d_p/D_m$, Sc = $\mu_w/\rho_w D_m$ and Re = $\rho_w u d_p/\mu_w$, in which the molecular diffusion coefficient D_m of methylene blue in aqueous solution is 3.6×10^{-10} m^2/s [27]. These values are substituted in Eq. (15) to evaluate K_f at different interstitial velocities in the mathematical model.

The axial dispersion coefficient calculated from Chung and Wen [28] equation:

$$\frac{D_b\rho_w}{\mu_w} = \frac{\text{Re}}{0.2+0.011\,\text{Re}^{0.48}} \tag{16}$$

4.3. Breakthrough curves

Figs. 5–8 show the experimental and predicted breakthrough curves for the methylene blue system onto Amberlite XAD4 at different adsorbent-glass beads weight ratios, flow rate, bed depth and initial concentration of adsorbate at constant temperature of 20°C. It is clear from these figures that

- Adding 5% glass beads weight ratio to the Amberlite XAD4 bed reduces its weight by 5% and increases the breakthrough time by 80%.

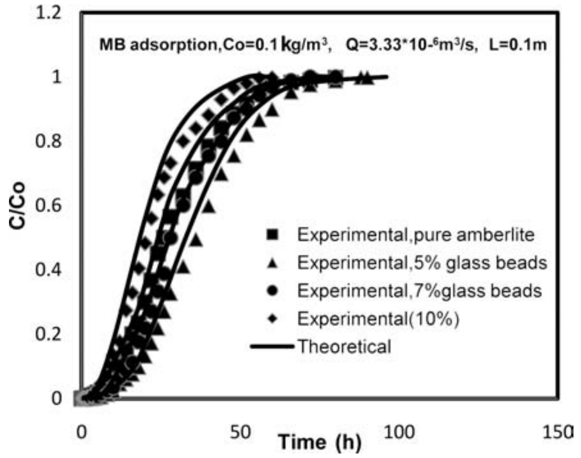

Fig. 5. Experimental and predicted breakthrough curves for MB adsorption onto Amberlite XAD4 at different glass beads weight ratios.

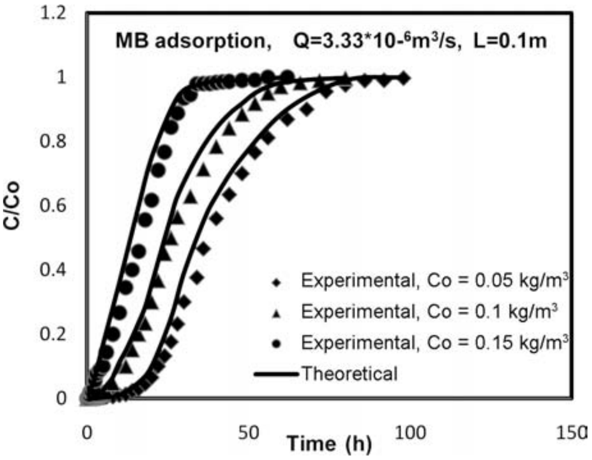

Fig. 6. Experimental and predicted breakthrough curves for MB adsorption onto Amberlite XAD4 at different initial concentrations.

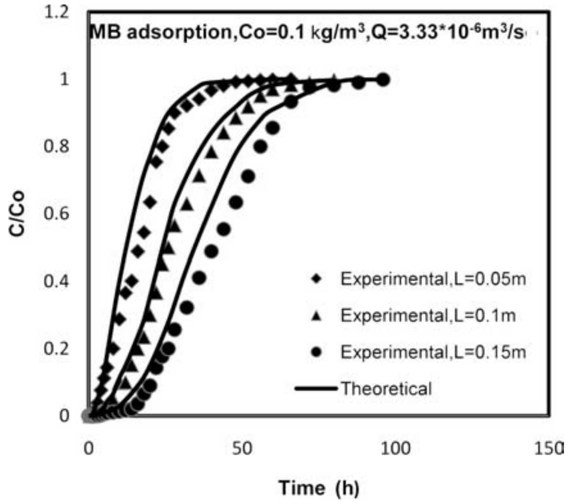

Fig. 7. Experimental and predicted breakthrough curves for MB adsorption onto Amberlite XAD4 at different bed depths.

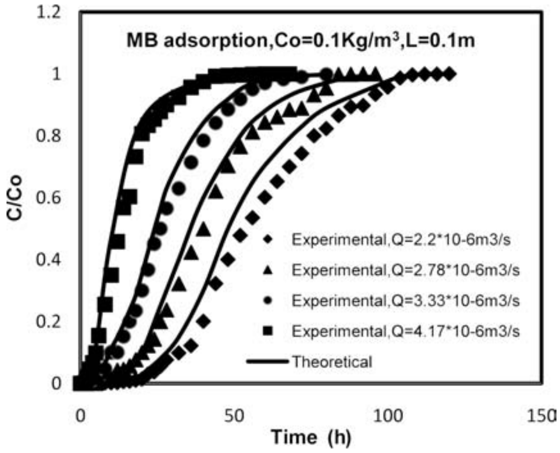

Fig. 8. Experimental and predicted breakthrough curves for MB adsorption onto Amberlite XAD4 at different flow rates.

- Adding 7% glass beads weight ratio to the Amberlite XAD4 bed reduces the weight of Amberlite by 7% and increases the breakthrough time by 20%.
- Increasing the glass beads ratios to 10% weight make the adsorption process is inefficient compared with 0% weight of glass beads. This may be attributed to the nature of Amberlite XAD4 particles, where it is entirely different from the glass beads regarding the roughness of the surface and the porosity of the material.

Consequently, changing the characteristics of the bed the glass beads have more or less smooth surface, while the Amberlite XAD4 particles have nearly rough surface (Fig. 9). Both pictures were taken by optical microscope of type Reichert-Jung, POLYVAR MET.

The liquid hold-up in a packed column is important for many reasons. It reduces the porosity of the packed bed [29]. Considering one Amberlite particle surrounded by many Amberlite particles in the bed, the contact surface which is covered by the static liquid hold up is large; probably cover the entire particle. Therefore, the presences of this particle will not be affected to the adsorption and can be ignored or replaced by inert material. This phenomenon can be occurred for many Amberlite particles in the bed. Since the static liquid hold up is stagnant and there is no mixing will occur with the operating liquid hold up. This will lead to increases the resistance to mass transfer and minimizing the surface of the Amberlite particles available for adsorption. Therefore, it is very essential to find the optimum amount of Amberlite particle which can be replaced by glass particles experimentally. From the above and from the principle of liquid hold-up, it can be concluded that static hold-up for adsorbent-adsorbent particles > adsorbent-glass beads > glass-glass beads.

This leads to the losses in surface area for adsorption as follows: Area losses in adsorbent–adsorbent particles > adsorbent–glass beads.

The dynamic liquid hold-up will have the same behavior as mentioned above; this is related to the differences in the nature of Amberlite XAD4 and the glass beads. Due to the roughness of the Amberlite XAD4 surfaces, the operating liquid film thickness will be higher for the adsorbent compared with glass beads for a given particle diameter, flow rate, pollutant concentration and temperature. Therefore the phenomena will lead to high resident time for the liquid on the adsorbents particles compared with glass particles, and consequently increases the breakthrough time for the adsorption process. The bed porosity increases for different adsorbent-glass beads weight ratios. The porosity is 0.36, 0.37, 0.38, and 0.4 for glass beads ratios 0, 5, 7, and 10% weight respectively.

- An increase in the initial concentration of methylene blue makes the breakthrough curves much steeper, which would be anticipated with the basis of increases driving force for mass transfer with the increase of concentration of adsorbate in the solution [30].
- An increase in the bed depth of Amberlite XAD4 will increase the breakthrough time and the residences time of the adsorbate in the column. An increase in the bed depth will increase Pe number with constant Bi number, where Pe number is the ratio of axial convection rate to axial dispersion rate. When Pe number is small (the effect of axial dispersion is not negligible)

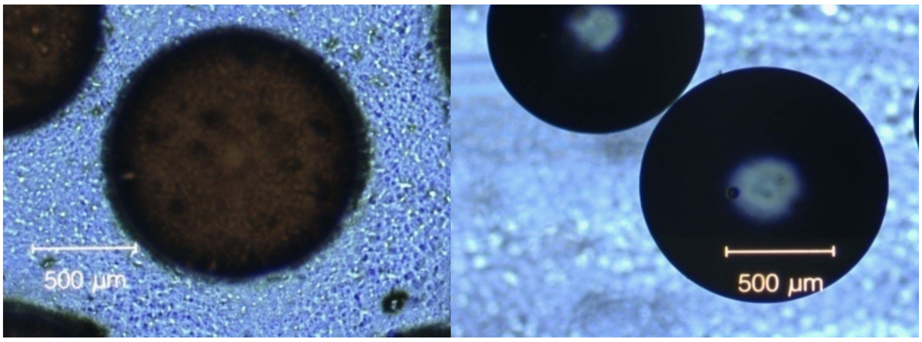

Fig. 9. Optical microscopic picture of Amberlite XAD-4 (left) and glass beads (right).

the breakpoint (the point at which breakthrough occurs) appears early and the breakpoint increases with increasing Pe number

- An increase in the adsorbate flow rate decreases the breakthrough time due to the decrease in the contact time between the adsorbate and the adsorbent along the adsorption bed. Increasing the flow rate may be expected to make reduction of the surface film. Therefore, this will decrease the resistance to mass transfer and increase the mass transfer rate. Also, because the reduction in the surface film is due to the disturbance created when the flow of the feed increased resulting of easy passage of the adsorbate molecules through the particles and entering easily to the pores. This will decrease contact time between the adsorbate and the adsorbent. An increase in the flow rate will increase Bi number and with slight increase Pe number. Bi number is the ratio of external mass transfer rate to the interparticle mass transfer rate (that is, the interparticle mass transfer is the control step) the breakpoint will appear early.
- The breakpoint was related to the flow rate, bed depth and initial concentration, i.e. the time required to reach breakpoint decreases with the increases of flow rate, decreases of bed depth, and increases of solute initial concentration.

5. Conclusions

The adsorption process can be made more efficient and/or economical by increasing breakthrough time via adding an inert material (glass beads) to Amberlite XAD4 bed in different weight ratios. The equilibrium isotherm data were correlated with five models, Langmuir model give the best fit for the experimental data. The batch experiments were helpful in estimating the isotherm model constants such as isotherm model constants, external mass transfer coefficient, and interparticle diffusion coefficient. There was a good matching between experimental and predicted data in batch experiment by using pore diffusion method. Hence the transfer of MB within the Amberlite XAD4 is controlled by pore diffusion. A general rate model which includes axial dispersion, film mass transfer, pore diffusion resistance and non-linear isotherms provides a good description of the adsorption process. An increase in the initial concentration of MB makes the breakthrough curves much steeper, which would be anticipated with the basis of increases driving force for mass transfer with the increase of MB concentration. The increase in the bed depth of Amberlite will increase the breakthrough time and the residence time of the MB in the column. While increasing the solute flow rate decreases the breakthrough time due to the decrease in the contact time between the adsorbate and the adsorbent along the adsorption bed.

Acknowledgment

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Symbols

A_R — Reddlich–Peterson model parameter
b — Langmuir constant, l/mg
Bi — Biot number ($k_f R_p/\varepsilon_p D_p$)
B_R — Reddlich–Peterson model parameter
C — Concentration in fluid, kg/m^3
C_o — Initial concentration, kg/m^3
C_e — Concentration of solute at equilibrium, kg/m^3
D_b — Axial dispersion coefficient, m^2/s
D_m — Molecular diffusion coefficient, m^2/s
D_p — Pore diffusion coefficient, m^2/s
d_p — Particle diameter, m
F_{RP} — Radke–Prausnitz model parameter
K — Freundlich empirical constant
k_f — Fluid to particle mass transfer coefficient, m/s
K_{RP} — Radke–Prausnitz model parameter
L — Length of bed, m
m_R — Reddlich–Peterson model parameter
N_{RP} — Radke–Prausnitz model parameter
n — Freundlich empirical constant
Pe — Peclet number (vL/D_b)
Q — Fluid flow rate, m^3/s
q_e — The amount of adsorbate per unit weight of carbon at equilibrium, kg/kg
q_m — Adsorption equilibrium constant defined by Langmuir equation, mg/g
Re — Reynolds number ($\rho_w v d_p/\mu_w$)
R_p — Radius of particle, m
Sc — Schmidt number ($\mu_w/\rho_w D_m$)
Sh — Sherwood number ($k_f d_p/D_m$)
T — Time, s
V — Interstitial velocity ($Q/A\varepsilon_b$), m/s
v_s — Superficial velocity (Q/A), m/s
V_L — Volume of solution, m^3
W_A — Mass of activated carbon, kg
Z — Axial distance, m

Greek

ε_b — Bed porosity
ε_p — Porosity of adsorbent
μ_w — Viscosity of water
ρ_w — Density of water, kg/m^3
ρ_p — Bulk density of amberlite, kg/m^3

References

[1] M.A. Haque, M.S. Un-Din and M. Haque, The effect of aqueous extracted wheat bran on the bading quality of biscuit, Int. J. Food Sci. Technol., 37 (2002) 453–462.

[2] D. Ozer, G. Dursun and A. Ozer, Methylene blue adsorption from aqueous solution by dehydrated peanut hull, J. Hazard. Mater., 144 (2007) 171–179.

[3] Material Safety Data Sheet, Spectrum, Gardena, CA, New Brunswick, NJ, 2006.

[4] Rohm and Hass, Amberlite XAD4, Preliminary Technical Notes, 1982.

[5] Rohm, and Hass, Amberlite XAD4 industrial grade polymeric adsorbent, Rohm and Hass Company, Philadelphia, 2003.

[6] A. Guzzella, D. Feretti and S. Monarca, Advanced oxidation and adsorption technologies for organic micropollutant removal from lake water used as drinking-water supply, Wat. Res., 36 (2002) 4307–4318.

[7] Y.C. Hsu, C.C. Chiang and M.F. Yu, Modeling and simulation for packed bed adsorption, Sep. Sci. Technol., 32 (1997) 2513.

[8] J.C. Crittenden and W.J. Weber, Predictive model for design of fixed bed adsorbers: parameter estimation and model development. J. Env. Eng. Div., ASCE, 104 (1978) 185.

[9] H.S. Shulman, C.F. Ulrich and N. Wells, Correlation of diffusion coefficients in dilute solutions, AIChE J., 1 (1955) 247.

[10] H.S. Shulman, C.F. Ulrich, N. Wells and A.Z. Proulx, Fluid-particle and intraparticle mass transfer rates in slurries, AIChE J., 1 (1955) 259.

[11] J.F. Davidson, E.J. Cullen, D. Hanson and D. Roberts, Mass transfer from freely suspended particle in stirred tanks, Trans. Inst. Chem. Eng., 37 (1959) 122.

[12] C.C. Furans and F. Bellinger,Mass transfer to particles suspended in agitated tanks, Trans. AIChE., 34 (1938) 251.

[13] J.C. Crittenden, J.K. Berrigan, D.W. Hand and B. Lykins, Design of rapid small-scale adsorption tests for a constant diffusivity. J. WPCF, 58(4) (1986) 312–319.

[14] T. Gu, Mathematical Modelling and Scale-up of Liquid Chromatography. Springer, Berlin, 1995.

[15] G. Guiochon, S.G. Shirazi and A. Katti, Fundamentals of Preparative and Nonlinear Chromatography. Academic Press, Boston, MA, 1994.

[16] D.M. Ruthven, Principles of Adsorption and Adsorption Processes. John Wiley and Sons, 1984.

[17] G. Ganetson and P.E. Barker, Preparative and Production Scale Chromatography. Marcel Dekker, New York, 1993.

[18] R. Eggers, Simulation of Frontal Adsorption. HIWI report by Hamburg-Hamburg University, 2000.

[19] P.M. Alexander and I. Zayas, Particle size and shape effects on adsorption rate parameters, J. Environ. Eng., 115(1) (1989) 41–55.

[20] B. Liu, Y. Yang and Q. Ren, Parallel pore and surface diffusion of levulinic acid in basic polymeric adsorbents, J. Chromatography A., 1132 (2006) 190–200.

[21] L. Ping, and X. Guohua, Competitive adsorption of phenolic compounds onto activated carbon fibers in fixed bed. J. Environ. Eng., 36 (2001) 730–734.

[22] J.R. Weber and J. Walter, , Physicochemical Processes for Water Quality Control. Wiley Interscience, New York, 1972.

[23] C.J. Radke and J.M. Prausnitz, Adsorption of organic compounds from dilute aqueous solution on activated carbon. Ind. Eng. Chem. Fundam., 11 (1972) 445–451.

[24] L. Jossens, J.M. Prausnitz and W. Frits, Thermodynamic of multi-solute adsorption from dilute aqueous solutions. Chem. Eng. Sci., 33 (1978) 1097–1106.

[25] R. Sips, A simplified method to design fixed-bed adsorber for Freundlich isotherm, J. Chem. Phys., 16 (1984) 490–495.

[26] S. Lucas and M.J. Cocero, Adsorption isotherms for ethylacetate and furfural on activated carbon from supercritical carbon dioxide. Fluid Phase Equilibria, 219 (2004) 171–179.

[27] MERCK Catalogue, Technical Data Sheet, KgaA, D-6421, Darmstadt, 2005, http://chemdat.mereck.de/mda/int_en/index.html.

[28] A. Gupta, O. Nanoti and A.N. Goswami, The removal of furfural from water by adsorption with polymeric resin. Separ. Sci. Technol., 36(13) (2001) 2835–2844.

[29] H.W. Cremer and T. Davis, Chemical engineering practice. Vol. 6, Fluid System II, Butterworths Scientific Publication, London, 1958.

[30] E. Malkoc and Y. Nuhoglu, Fixed bed studies for the sorption of chromium (VI) onto tea factory waste. Chem. Eng. Sci., 61 (2006) 4363–4372.