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# Experimental Study and Adsorption Modeling of COD Reduction by Activated Carbon for Wastewater Treatment of Oil Refinery

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**ABSTRACT:** *Application of Granular Activated Carbon (GAC) in adsorption process has been studied for the advanced treatment of municipal and industrial wastewater. Because of entering poisonous compounds such as furfural, phenol and sulfides into the oily wastewater of Tehran refinery, biological aeration basins of wastewater treatment unit may not have the desired performance of COD reduction. In this study, GAC is examined for reduction of COD effluent from the Dissolved Air Flotation (DAF) unit to achieve to the environmental and design regulations. The equilibrium batch experiments as well as dynamic adsorption tests were performed to determine the maximum adsorption capacity and the breakthrough curves of COD, respectively. The data derived from equilibrium studies were modeled using Langmuir theory and the isotherm parameters were determined at two different temperatures of 25 and 40 C. Dynamic adsorption modeling was carried out considering the axial dispersion model in the bed of GAC with the assumption of lump kinetic mass transfer and linear driving force into the solid phase. The model results of COD breakthrough curve concentration have shown a fairly good agreement with experimental results. The sensitivity analysis of the dynamic model was carried out at different temperatures, bed lengths, feed flow rate and feed concentration to have a proper insight for appropriate design of a GAC fixed bed. It is concluded that GAC fixed bed could be an auxiliary unit for biological treatment of wastewater to overcome the problems of biological basin in oil refineries.*

**KEY WORDS:** *Granular Activated Carbon (GAC), Adsorption, Breakthrough curve, Dynamic modeling, COD removal, Oily waste water.*

## INTRODUCTION

Oily waste water is a byproduct of many industrial and small quantity generator commercial operations. Refineries are high water consumers and consequently large waste water producer. Good quality water is often required in order to comply with environmental and design regulations. Additionally, in areas of limited water resources, water economics may dictate the possible reuse of wastewater effluent. Such consideration requires the efficient treatment of the waste water for the removal of hazardous contaminants. The organic content of waste water is traditionally measured using lumped parameters such as Biological Oxygen Demand (BOD), Chemical Oxygen

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Demand (COD), and Total Organic Carbon (TOC) [1-3]. Various physicochemical and microbiological treatment methods have been implemented for the treatment of oily waste waters [4,5].

The treatment system of refinery wastewaters includes pretreatment by gravity oil separator followed by Flocculation and Dissolved Air Flotation (DAF) to reduce the suspended solids as well as oil and grease. Additionally, removal of dissolved organics requires biological treatment or physicochemical treatment. A variety of modifications to conventional biological treatment methods has been suggested and evaluated in bench, pilot and full-scale systems [6-9].

The Environmental Protection Agency (EPA) stated that there is ample evidence in the literature to suggest that adsorption process by porous materials would be considered as an alternative for the petroleum refinery waste water treatment when the biological system is encountered with problem [10-12].

Adsorption of organics and contaminants by AC are widely studied for wastewater treatment [1-3, 6, 13-16]. Majority of these researches are focused on synthetic feed models made from specific organic materials [6,15] and some of the literatures have been working on equilibrium and kinetic studies of COD and BOD adsorption from the wastewaters [1-3,13,14,16]. In these studies the equilibrium models and their parameters are reported for the single pseudo-component on the base of simple and practical isotherms such as Langmuir, Frendlicsh. In the kinetic studies it has been found that film resistance has significant effect for transfer of low concentration matters from liquids to the solid, linear and quadratic driving forces are the most popular lump kinetic models [1]. Rare studies are focused on dynamic studies of continuous wastewater flow through the adsorbent beds for COD adsorption from wastewaters [2,16]. Although none of these studies are focused on dynamic modeling of the packed beds for COD removal. The experimental and modeling study in batch and fixed bed column accompanied with dynamic modeling of COD adsorption from DAF has been performed in the present study.

In this work, GAC fixed bed adsorption unit has been proposed and modeled for COD removal as an alternative of biological treatment to control the COD of the waste water unit in emergency conditions to achieve the COD effluent standard (less than 200 ppm) and design regulation of COD effluent (less than 100 ppm). In this research, COD analysis is chosen as a standard method of measurement to come across the ability of organics removal by GAC from the oily waste water. The dynamic adsorption of the organics is modeled using COD as the lump contaminant by the axial dispersion model and film mass transfer resistances during the movement of the feed along the GAC bed. Simulation of the real feed COD of the oily wastewater from DAF unit of Tehran Refinery is carried out by the commercial Iranian made AC to approach to the desired level.

## WASTE WATER TREATMENT UNIT OF TEHRAN REFINERY

Waste Water Treatment Unit (WWTTU) of Tehran Refinery was designed to treat 7600m3/day of oily waste water in which process units discharge waste water to oily water pipes. Also, WWTTU was designed by Fluor Company at 1977 in order to remove free and emulsified oil for getting water which can used as a makeup in cooling towers. Also, there are three steps for oily waste water treatment which contains physical, chemical and biological treatments. The first step in oily waste water unit of Tehran refinery is the physical treatment that the bulk of oil is removed by American Petroleum Institute (API) separators. These separators are designed to remove oil droplets down to 150 microns in size and the typical effluent concentrations achieved are greater than 100 ppm. Also, API separation systems were designed for free floating oil which would be ineffective in dealing with a wastewater containing primarily emulsified oil. If the waste water from a small quantity generators operation contains a stable emulsion of oil in water, the waste water must be treated by chemical in order to reduce oil. In particular sense, breaking the emulsion would result in one of two possible outcomes. In biological treatment section, there are three basic biological oxidation activated sludge process. At waste water treatment unit of Tehran Refinery, aeration basins are completely mixed activated sludge process. The DAF process consists of pressurizing a waste flow and dissolving air at elevated pressure up to 60 psig followed by release to atmospheric pressure and the dissolved air is released in the waste stream in extremely fine bubbles. For the sake of, entering high amount of free oil, toxic compounds such as furfural, phenol and sulfides into the oily wastewater of Tehran refinery, biological aeration basins of wastewater treatment unit are not able to provide effluent water with COD concentrations which are less than 100 for design speck or than 200 ppm for agriculture irrigation. The low temperature during the winter could be another inhibition factor against biological treatment at the desired level.[12]

## THEORITICAL SECTION

### *Adsorption process*

In the situations of bad working of biological treatment, an adsorption unit with appropriate amount of AC is required to be designed and constructed in parallel of the biological unit for conduction a part of wastewater after DAF into these columns as the auxiliary section for COD reduction.

There are many parameters and properties which have to be determined before design of an adsorption unit. Some important parameters are adsorbed capacity, adsorption isotherms and mass transfer parameters of AC for COD [16,17].

Selection of AC, derivation of equilibrium isotherms, dynamic adsorption model and sensitivity analysis of COD breakthrough curves are the issues which have been conducted in following sections to get the reliable results for scale up and design of adsorption unit.

### Dynamic model development

The dynamic adsorption model formulation in a fixed bed was developed for COD adsorption of wastewater on the studied AC.[17,18] The model is assumed a dispersed plug flow with lumped mass transfer resistance with solid linear driving force into the particles. The model assumptions are as following:

1. The system operates under isothermal conditions.
2. The adsorbent particles are spherical and uniform with homogenous porosity.
3. The pressure drop throughout the column is negligible.
4. Because of low COD concentration in fluid the velocity variation along the bed is ignored.
5. The inter- mass transfer and intra-particle pore diffusion have been taken into account with overall mass transfer resistance.
6. Lumped mass transfer resistance with solid Linear Driving Force (LDF) is considered for kinetic adsorption of COD into the particles [18].
8. The overall mass transfer coefficient is tuned with experimental results of the fluid breakthrough curve.
7. The maximum adsorbed capacity and isotherm parameters of AC is explained by Langmuir isotherm and obtained from equilibrium experiments.

By the above assumptions, the COD mass balance is a model molecule is derived in the bed of AC as following:

$$-\frac{1}{\mathrm{Pe}}\frac{\partial^2 \bar{C}}{\partial \bar{z}^2}+\frac{\partial \bar{C}}{\partial \bar{z}}+\frac{\partial \bar{C}}{\partial \bar{t}}+\frac{(1-\varepsilon)\rho_P q^*}{\varepsilon}\frac{\partial \bar{q}}{\partial \bar{t}}=0 \qquad (1)$$

$$\mathrm{Pe}=\frac{uL}{D_z},\quad \bar{t}=\frac{ut}{L},\quad \bar{z}=\frac{z}{L},\quad \bar{C}=\frac{C}{C_0},\quad \bar{q}=\frac{q}{q^*}$$

The following initial conditions can be considered in adsorption model:

$$\bar{C}(\bar{z},0)=0 \qquad (2)$$

$$\bar{q}(\bar{z},0)=0 \qquad (3)$$

The boundary conditions at both ends of the column are given by following equations:

$$\bar{C}(0,\bar{t})=1+\frac{1}{\mathrm{Pe}}\frac{\partial \bar{C}(0,\bar{t})}{\partial \bar{z}} \qquad (4)$$

$$\frac{\partial \bar{C}(1,\bar{t})}{\partial \bar{z}}=0 \qquad (5)$$

Intra-particle mass transfer can be described by the LDF model. This model is frequently used for this purpose because it is analytical, simple and physically consistent. According to the solid LDF model, the rate of adsorption of COD as a psedue-component into the adsorbent is given by:

$$\frac{\partial \bar{q}}{\partial \bar{t}}=\frac{Lk_n}{u}\left(1-\bar{q}\right) \qquad (6)$$

Where $q^*$ is the max. adsorbed concentration in the solid phase and the $k_n$ is the overall mass transfer coefficient which is related to internal and external mass transfer resistance:

$$\frac{1}{k_n}=\frac{R_p}{3k_f}+\frac{R_p^2}{15D_p^e\varepsilon_p} \qquad (7)$$

The adsorption capacities were deduced from equilibrium adsorption isotherms using the Langmuir

***Table 1: Removal efficiency of COD from DAF unit effluent by different ACs and the price.***

| | LGAS 85 | Aquasorb 1000 | Aquasorb 2000 |
|---|---|---|---|
| COD reduction% | 79% | 77% | 80% |
| Unit Price(Rials/kg) | 20,000 | 77,000 | 80,000 |

isotherm model. The validity of this model for the representation of the COD equilibrium data will be later explained in detail.

$$q^* = \frac{bC}{1+kC} \qquad b = kq_{\infty} \tag{8}$$

The film mass transfer coefficient, $k_f$, was calculated from the following correlation [17]:

$$SH = 2 + 1.1(Sc)^{0.33}(Re)^{0.6} \tag{9}$$

Where Sh, Sc and Re are respectively the Sherwood, Schmidt and Reynolds numbers of the fluid and $k_f$ can be directly obtained from the Sh number. The effective diffusivity ($D_p^e$) was determined from the following equation [17]:

$$D_p^e = \frac{D_m}{\tau_p} \tag{10}$$

Molecular diffusivity of COD as a model molecule ($D_m$) was determined by fine tuning the experimental data with the mathematical model using the computer program. Tortousity factor of the AC was calculated as following [17]:

$$\tau_p = 1/\varepsilon_p \tag{11}$$

Axial dispersion coefficient, $D_z$, was calculated from the following correlation[17]:

$$\frac{D_x}{D_m} = \gamma_1 + \gamma_2 \frac{(Re).(Sc)}{\varepsilon} \tag{12}$$

Where:

$$\gamma_1 = \frac{20}{\varepsilon} \qquad \gamma_1 = 0.5 \tag{13}$$

### *Solution Technique*

Since nonlinear adsorption equilibrium is considered, the preceding set of differential equations is solved numerically by a Method of Line technique. The numerical algorithm is developed and implemented into a computer program using MATLAB (R.2007b) software.

## EXPERIMENTAL SECTION

### *Selection of appropriate activated carbon*

To choose the best AC for adsorption unit, three kinds of available and commercial AC attributed with LGAS 85, AQUASORB 2000, AQUASORB 1000, were chosen and examined, comparatively, in batch experiments for two hours contacting time, at the constant temperature of 25 ºC, on the output effluent of the Dissolved Air Flotation (DAF) unit of oil refinery. The first one was an Iranian commercial AC from Shimi Pajohan Co., whereas the other two ACs were taken from Nurit Co.

The results of COD removal efficiencies are presented in Table 1 with the unit price of each AC product.

The results showed that the performance of three kinds of AC was almost identical and removal efficiency was obtained around 80%. By considering the unit price of the ACs, LGAS 85 which is an Iranian commercial product with a price of one fourth of the others was selected for detail studies.

### *Batch and Equilibrium Experiments*

Outlet wastewater from DAF unit was tested for reduction of COD by LGAS 85 to figure out the performance of AC in oil refinery waste water treatment.

To determine the equilibrium adsorption model, various samples with different concentrations were mixed mechanically in 150 ml of the waste water with five grams GACs at 200 rpm and 25 ºC. Solutions were filtered through a filter and the fraction of COD removal was determined by measuring the COD remaining in solution using dichromate reflux method. The results showed that it takes around 2 to 3 h to achieve the equilibrium condition. The maximum adsorption capacities of AC were determined at two different temperatures of 25 °C and 40 °C. By these studies, two isotherms were obtained to derive the equilibrium model and its parameters.

### *Dynamic Experiments*

Industrial adsorption systems mostly use fixed bed columns of adsorbent for their treatment process. In actual practice, it is mostly the columns which are used

***Table 2: Operational conditions of the dynamic adsorption.***

| | | | |
|---|---|---|---|
| $C_0$ | Inlet COD | 420 | $g/m^3$ |
| $d_b$ | Column diameter | 0.01 | m |
| L | Column length | 0.23 | m |
| w | Adsorbent weight | $6.5\text{x}10^{-3}$ | kg |
| T | Temperature | 298.15 | K |
| $u_0$ | Superficial linear velocity | 0.0024 | m/s |
| $\varepsilon$ | Bed porosity | 0.32 | - |
| $\rho_b$ | Bed density | 360 | $kg/m^3$ |
| $\upsilon_o$ | Superficial inlet flow rate | $0.185\text{x}10^{-6}$ | $m^3/s$ |

***Table 3: Model parameters of dynamic adsorption modeling.***

| | | | |
|---|---|---|---|
| $D_z$ | Axial dispersion coefficient | $1.05\text{x}10^{-5}$ | $m^2/s$ |
| $D_m$ | Molecular diffusion coefficient | $1.2\text{x}10^{-10}$ | $m^2/s$ |
| $k_f$ | External film mass transfer coefficient | $1.83\text{x}10^{-6}$ | m/s |
| $R_p$ | Radius of the adsorbent pellets | 0.0005 | m |
| $\varepsilon_p$ | Porosity of the adsorbent pellet | 0.4 | - |
| $\rho_F$ | Solution density | 1000 | $kg/m^3$ |
| $\rho_p$ | Particle density | 530 | $kg/m^3$ |
| $\tau$ | tortousity factor of adsorbent | 2.5 | - |
| $\mu$ | Solution viscosity | 0.93 | cp |

for the adsorption of pollutants from waste water. Adsorption isotherms obtained from batch experiments could not possibly give accurate scale-up information for several reasons [17]:

1. Adsorption in a flow column is not at equilibrium.
2. The adsorbent would not become totally exhausted in a commercial process before regeneration.
3. Flow patterns throughout the column would result in incomplete exhaustion of the bed.
4. The effects of sorbent recycling and regeneration could not be studied and isotherms could not predict changes occurring in the adsorber.

Therefore it is necessary to survey dynamic condition using dynamic flow studies in the bed. The dynamic studies were performed using a glass column with 0.01 m diameter and 0.23 m height, to determine the adsorption breakthrough curves. Initial concentration of feed was 420 ppm COD, temperature was kept constant at 25 °*C* and the column was filled with 6.5 gr of LGAS 85. The solution flow rate through the column was maintained at $0.185\text{x}10^{-6}$ $m^3/s$. Schematic diagram of the GAC fixed bed set up is observed in Fig. 1. The operational conditions and parameters are reported in Table 2 and 3, respectively.

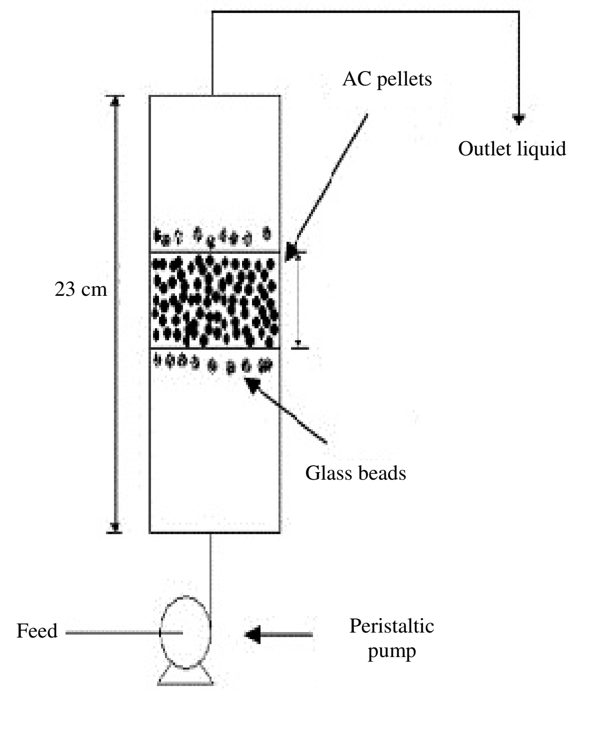

***Fig. 1-Schematic of GAC packed bed set up.***

*Table 4: Langmuir adsorption model parameters in each temperature*

| Parameter / Temperature | k ($m^3/g_{Adsorbed}$) | b ($m^3/kg_{Adsorbent}$) | $r^2$ |
|---|---|---|---|
| 25 °C | 0.35 | 0.87 | 0.98 |
| 40 °C | 0.32 | 0.66 | 0.97 |

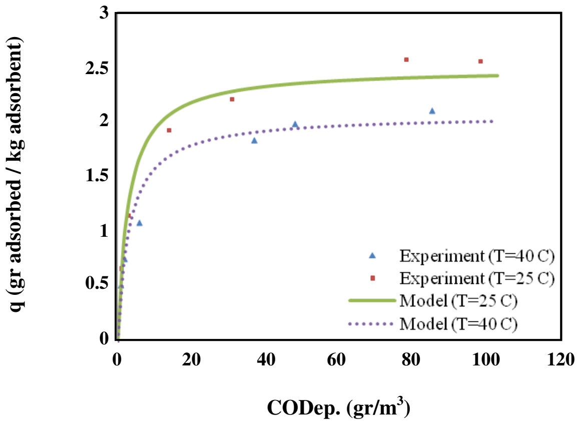

*Fig.2: Adsorption isotherms of COD on AC.*

## RESULT AND DISCUSSION

### *Isotherm Model*

Analysis of COD in each test run, was carried out on the base of standard dichromate reflux method (ASTM D1252-06). Some of the experiments were performed for testing the replication of the results. The results of adsorbed COD versus equilibrium COD of solution were obtained at two constant temperatures and they are shown in Fig. 2 for the real wastewater.

Four different models were applied to fit the experimental results; Langmuir, Frendlich, Toth and Sips. Among these models, the experimental isotherms were properly fitted to the Langmuir model using the following equation:

$$q^* = \frac{bC}{1+kC} \tag{14}$$

$$b = kq_\infty$$

Where q* is the equilibrium adsorbed capacity, C is equilibrium COD in solution, b and k are the Langmuir parameters at a particular temperature. The corresponding isotherm parameters were determined by regression analysis obtaining a linear expression for Langmuir equation.

Table 4 shows the parameters b, k and coefficient of determination obtained from regressed isotherm data on Langmuir model.

The Average Absolute Relative Deviation (AARD) of the adsorbed COD between the model and experiments is determined as 7% at temperature of 25°*C* and 10% at temperature of 40 °*C*. As a result it is concluded that Langmuir isotherm with derived parameters is a reasonable isotherm model for COD adsorption of the oil refinery wastewater in temperature range of 25 to 40 °*C*. The constants of each parameter are calculated using Arrhenius' equation as an exponential function of temperature in Eqs. (15) and (16).

$$b = 2.5\times10^{-3}\exp(\frac{1741.1}{T}),\ m^3 / kg_{Adsorbent} \tag{15}$$

$$k = 0.054\exp(\frac{559.6}{T}),\ m^3 / g_{Adsorbed} \tag{16}$$

### *Dynamic Model*

#### *Model Validation*

The dynamic model determines the breakthrough curve of COD based on the operating conditions and adsorbent properties. Bed characteristic, operating conditions and physical properties are shown in Tables 2 and 3. Fig. 3 shows the breakthrough curve obtained from dynamic experiment and the model at 25°*C*. It can be observed that both breakthrough results, model and experiment, are approximately close to AARD of 26%.

The dynamic model can be used for interpretation of the results for the proper design of the AC packed columns working at specific operating conditions. In this work, the residence time of the feed is 1.5 min and the breakthrough time of the COD effluent is obtained 10 min, as shown in Fig. 3, whereas *Ademiluyi et al.* achieved 50 min breakthrough time in their experiments for 24 min feed residence time (16 fold more than our work) with similar inlet COD conditions. It is revealed that the efficiency of LGAS 85 is much more higher than their AC made from *Nigerian Bamboo* [16].

To have proper insight to the design of adsorption units, the effect of operating conditions should be investigated by the sensitivity analysis of the dynamic model.

Operating conditions such as feed flow rate, bed and inlet temperature, bed length and adsorbent weight, inlet wastewater concentration are the significant factors for determination the bed capacity and breakthrough time of the effluent. Finally, the present model has been examined and evaluated in sensitivity analysis towards variation of operating conditions.

### *Model Sensitivity analysis*

### Effect of flow rate

The results for different solution flow rates are plotted for a bed height of 0.23 m and an inlet COD concentration of 420 ppm at temperature of 25°C in Fig. 4. The results show that with increasing the flow rate, the breakthrough time decreases. This is because of the residence time of the solute in the column which is not long enough for adsorption equilibrium to be reached at high flow rates. Furthermore, saturation capacity of the bed based on the same driving force gives rise to a shorter time for saturation at higher flow rate.

### Effect of bed height

The effect of bed height on the effluent COD concentration is presented for flow rate of 0.0024 m/s and inlet COD of 420 ppm at 25°C in Fig. 5. It is observed that as the bed height increases, the breakthrough time is appeared later. Furthermore, the bed is saturated in less time for smaller bed heights, the smaller bed height corresponds to less amount of adsorbent.

### Effect of Temperature

The effect of temperature on effluent concentration is shown in Fig. 6. The considered temperatures are 25, 30 and 40 °C. The other parameters such as flow rate, bed height and inlet COD concentration are kept constant. Figure 5 reveals that as the temperature increases from 25 to 40 °C, the breakthrough time decreases because the adsorption is an exothermic process, increasing the temperature has an inverse effect on the efficiency of the process.

### Effect of inlet concentration

The effect of inlet COD on effluent concentration is shown in Fig. 7. In these simulations other parameters such as temperature, flow rate and bed height are kept constant. It is observed that at higher inlet concentration the breakthrough time is decreases. For higher feed

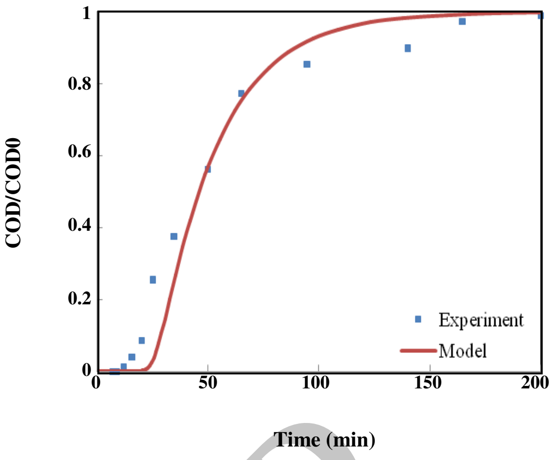

*Fig. 3: Experimental and model breakthrough curves.*

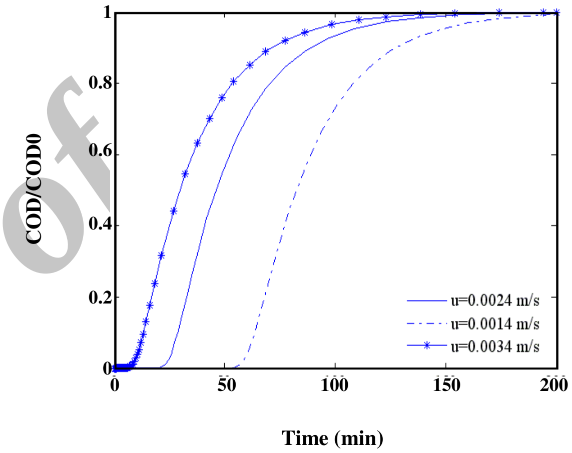

*Fig. 4: Effect of flow rate on breakthrough curve, by model.*

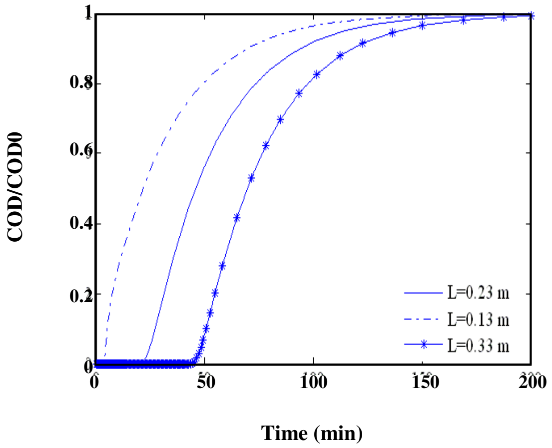

*Fig. 5: Effect of bed height on breakthrough curve, by model.*

concentration, steeper breakthrough curves are encountered, because of the lower mass transfer flux from the bulk solution to the particle surface due to the weaker driving force. In addition, at high concentration, the isotherm gradient is smaller, yielding a higher driving force to the adsorbent. Thus the equilibrium is attained faster for values of higher COD concentration.

## CONCLUSIONS

It is concluded that LGAS 85 would be an appropriate alternative for reduction of the COD of oil refinery waste water to approach to the design and environmental regulations and whenever the outlet effluent of the wastewater treatment unit does not comply environmental standards and regulations, adsorption unit could be a suitable auxiliary unit.

The isotherm model for COD of refinery waste water is described by Langmuir equation and its parameters have been predicted for LGAS 85 in the temperature range of 25 to 40 °*C*. This type of isotherm can be used in developed dynamic adsorption model in scale up and design of the adsorption unit in oil refineries for waste water treatment.

For dynamic condition a generalized model that incorporates external film mass transfer resistance and axial resistance through the packed bed has been formulated and solved numerically. The obtained results have shown a fairly good agreement with experimental data.

To scale up the adsorption unit for reduction of COD to less than 100 ppm, for working at ambient temperature with an inlet COD concentration of 420 ppm, a bed with 12 m height and 1 m diameter should be designed for treating 338 $m^3$/hr wastewater, keeping liquid hourly space velocity at the level of 0.01 $S^{-1}$. In this situation the predicted outlet COD concentration from the AC bed is remained lower than 100 ppm during two hours running the adsorption process. The present model is an efficient tool for designing the auxiliary process of the biological unit for reduction and removal of COD of the effluent from oil refineries.

### Nomenclature

| | |
|---|---|
| A | Area of cross section, $m^2$ |
| C | Bulk phase COD concentration, $g/m^3$ |
| $C_0$ | Inlet adsorbate concentration, $g/m^3$ |
| $d_b$ | Column diameter, m |
| $D_p^e$ | Effective pore diffusion coefficient, $m^2/s$ |
| $D_z$ | Axial dispersion coefficient, $m^2/s$ |
| $D_m$ | Molecular diffusion coefficient, $m^2/s$ |
| k | Langmuir isotherm parameter, $m^3/g$ |
| $k_f$ | External film mass transfer coefficient, m/s |
| $k_n$ | Overall mass transfer coefficient, 1/s |
| l | Column length, m |
| q | Concentration adsorbed on the surface of adsorbent, g/kg |
| q* | Equilibrium adsorption capacity, g/kg |
| $q_\infty$ | Langmuir isotherm parameter, g/kg |
| $R_p$ | Radius of the adsorbent pellets, m |
| t | Time, sec |
| T | Temperature, K |
| u | Superficial velocity, m/s |
| z | Axial coordinate, m |

### Dimensionless numbers

| | |
|---|---|
| Re | Reynolds number |
| Sc | Schmidt number |
| Sh | Sherwood number |

### Greek symbols

| | |
|---|---|
| $\varepsilon$ | Bed porosity |
| $\varepsilon_p$ | Porosity of the adsorbent pellet |
| $\rho_F$ | Solution density, $kg/m^3$ |
| $\rho_p$ | Particle density, $kg/m^3$ |
| $\rho_b$ | Bed density, $kg/m^3$ |
| $\tau$ | Pore tortuosity |
| $\mu$ | Solution viscosity, cp |
| $\upsilon_o$ | Inlet flow rate, $m^3/s$ |

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