

ADSORPTION PROCESS ON FIXED BED COLUMN IN RICH ORGANIC WASTEWATER TREATMENT- EXPERIMENTAL STUDIES AND NUMERICAL SIMULATION

NGUYEN HONG KHANH, NGUYEN VIET HOANG

*Institute of Environmental Technology
Vietnamese Academy of Science and Technology*

Abstract. None axially dispersed plug flow model (NADPF) was applied to simulate adsorption process on fixed bed column. To determine model input parameters and verify the model, isotherm curve, solid diffusion coefficient (D_s) and breakthrough curve have been determined from experiment. Activated carbon SWW 210&220 was selected as the main adsorbent for research. Wastewater of Minhkhai Textile Company is the sample used in experiment study. According to isotherm function, textile wastewater is poorly adsorbed into SWW210&220. Kinetic data also show that diffusion step of textile wastewater is very slow ($D_S \sim 1.31 \cdot 10^{-13} \text{ m}^2/\text{s}$). With textile wastewater, NADPF model can be used to simulate adsorption process.

Keywords: adsorption, simulation, activated carbon, textile wastewater.

1. INTRODUCTION

Adsorption is one of the most important methods used to treat the liquid pollutants, especially the non-biodegradable substances (ex. textile wastewater) [5]. Although, the effect of this method is quite high and it may be applied in many cases in that the conventional methods are difficult to be used [6], its application is still limited. An important reason is high price of the adsorbents. Many researchers have focused on the study for finding adsorbents of low price, but these studies are still in laboratory scale. An another approach is to optimize the design and operation of adsorption process. In the framework of fundamental research program in the field of Mechanics, in the Institute of Environmental Technology, Vietnamese Academy of Science and Technology, series of experiment studies and numerical simulation work on a rich organic wastewater by adsorption process have been realised. The equipment for adsorption is the fixed bed column and Jatest and the adsorbent is activated carbon. The sample in research is wastewater of MinhKhai Textile Company. The aim of this paper is to describe the comparison of the results of experiment and simulation through the two experiments carried out in the lab.

2. NUMERICAL SIMULATION

2.1 Mathematical Model of Adsorption Fixed Bed Column

None axially dispersed plug flow model (NADPF) was applied to simulate adsorption process on fixed bed column. According to [4, 8], this model can be used for simulating the adsorption process of liquid-solid. The model includes two partial differential equations. The equation (2.1) describes the material balance of column, and the equation (2.2)

describes the accumulation rate of the components in the solid phase with the concept that solid diffusion is of a limited step.

$$\frac{\partial c}{\partial t} + \frac{\rho}{\varepsilon} \frac{\partial q}{\partial t} + v \frac{\partial c}{\partial x} = 0, \quad (2.1)$$

$$\frac{\partial q}{\partial t} = \frac{15D_s}{r^2}(q^* - q), \quad (2.2)$$

where: c : pollutant concentration in liquid phase (mg/l); D_s : solid diffusion coefficient (dm^2/h); q : pollutant concentration in solid phase (mg pollutant per g activated carbon); q^* : pollutant concentration in solid phase at equilibrium state (mg pollutant per g activated carbon); r : activated carbon radius (dm); t : time (hr); v : liquid velocity in adsorption column (dm/hr); x : axial coordinate; ρ : specific weight of activated carbon (g/l); ε : void fraction.

2.2 Input parameters of Model

a. Liquid velocity and technical specifications of activated carbon

Liquid velocity is determined by pump. Technical specification of activated carbon is supported by producer [9].

b. Equation of adsorption isothermal curve (q^*)

In the adsorption liquid-solid process, there are two widespread equations for adsorption isothermal curve that are the equation of Langmuir (2.3) and Freundlich (2.4). The suitable type of adsorption isotherm equation will be selected by the compatibility with experimental results. From this, value of coefficient a , b , K and m are also determined.

$$q^* = \frac{abc}{1 + bc}, \quad (2.3)$$

$$q^* = Kc^m, \quad (2.4)$$

where: a , b : coefficients determined by experiments; c : pollutant concentration in liquid phase (mg/l); K : velocity of adsorption process determined by experiments; m : coefficient determined by experiments; q^* : pollutant concentration in solid phase at equilibrium state (mg pollutant per g activated carbon).

c. Solid diffusion coefficient (D_s)

According to [3], value of D_s is calculated from equation (2.5). It presents the linear relation between q/q^* and $t^{0.5}$ with the slop coefficient of $6(D_s/\pi R^2)$. Therefore, from the kinetic data, value of D_s can be determined easily.

$$\frac{q}{q^*} = 6\left(\frac{4D_s t}{\pi d^2}\right)^{0.5}, \quad (2.5)$$

where: q : pollutant concentration in solid phase (mg pollutant per g activated carbon); q^* : pollutant concentration in solid phase at equilibrium state (mg pollutant per g activated carbon); D_s : solid diffusion coefficient (dm^2/h); d : average diameter of activated carbon (dm); t : time (hr).

2.3 Solution Method

To find out solution for the model (described by equation 2.1 and 2.2), set of partial differential equations is converted to set of ordinary differential equations - ODEs. And after that, ODEs are solved by ODE15s program (MATLAB 7.0). Boundary and initial conditions are included:

Initial conditions: $c(0, x) = q(0, x) = 0$;

Boundary conditions: $c(t, 0) = c_0$ and $\frac{dc(t, H)}{dx} = 0$ (H is the length of bed).

After solving model with the above boundary and initial conditions, obtained results are concentration distribution in liquid and solid phase in time and length of column.

3. EXPERIMENT AND RESULT

3.1 Experiment

The purposes of experiment are to determine input parameters for the model (including isotherm curve and solid diffusion coefficient) and to construct breakthrough curve (used for model validation).

3.1.1 Material and Equipment

Asorbent for research is activated carbon, commercially named SWW210 & 220 [9]. Water sample is wastewater of MinhKhai Textile Company. Used equipments are Jartest and fixed bed adsorption column ATA2 (Fig. 1).



Fig. 1 . Jartest and fixed bed adsorption column ATA2

3.1.2 Experiment programs

With the above purposes, two experiment programs were done in laboratory:

Experiment program 1: determining input parameters for model such as: isotherm curve and solid diffusion coefficient (carried out in Jartest equipment).

Experiment program 2: constructing breakthrough curve for model validation (carried out in adsorption fixed bed column ATA2 with down - flow mode).

3.1.3 Analysis method

For assessing the treatment efficiency, concentration of COD (chemical oxygen demand - mg/l) is selected for textile wastewater and analyzed according to Standard Method No. 5220C [1].

3.2 Experimental results

3.2.1 Isotherm curve

Fruendlich equation is changed to logarithm form and Langmuir one is transferred to inversion form. The relationship between $\log(q)$ and $\log(c)$ or $1/q$ and $1/c$ has the form

of line ($y = Ax + b$ (Table 1)). Value of coefficients in Freundlich and Langmuir equation is calculated from this.

Table 1. Fitting experimental data with isotherm model

Sample	Fruendlich	Langmuir
ISOT1	$y=5.2279x-8.5992$ ($R^2=0.917$)	$y=1.5943x-0.0088$ ($R^2=0.981$)
ISOT2	$y=4.7543x-8.7984$ ($R^2=0.989$)	$y=4.9787x-0.0176$ ($R^2=0.939$)

where: R^2 is squared value.

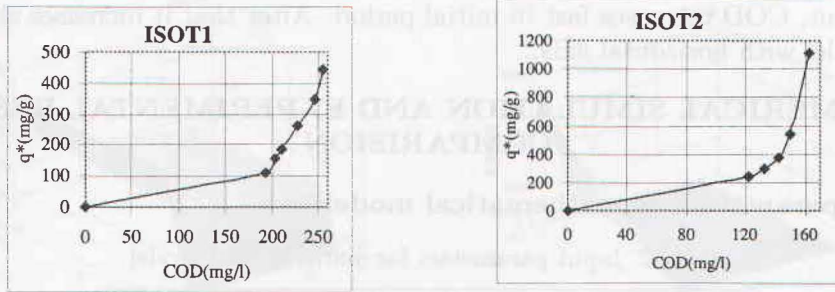


Fig. 2. Relationship between concentration in liquid and solid phase at equilibrium state

Experimental results include two sets of data ISOT1 and ISOT2. These results show that isotherm curves are concave (Fig. 2); it means adsorption is unfavorable. At small concentration, isotherm curves are nearly linear (COD<200 mg/l with ISO1-Fig. 2 and COD<150mg/l with ISOT2-Fig. 2). Curve slope varies normally. After fitting experimental data with isotherm model (Table 1), the Fruendlich equation is able to represent experimental data with reasonable accuracy (equation 3.1 and 3.2). The Langmuir equation cannot be used because in this case value of coefficient a in equation (2.3) is negative.

$$\text{ISOT1: } q^* = 2.5 \cdot 10^{-9} \text{ COD}^{5.2279} (R^2 = 0.9171) \tag{3.1}$$

$$\text{ISOT2: } q^* = 1.5 \cdot 10^{-9} \text{ COD}^{4.7545} (R^2 = 0.989) \tag{3.2}$$

3.2.2 Experimental result for determining D_s

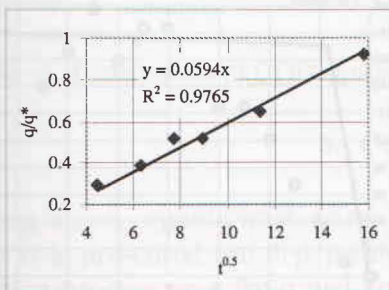


Fig. 3. Relation ship between q/q^* and $t^{0.5}$

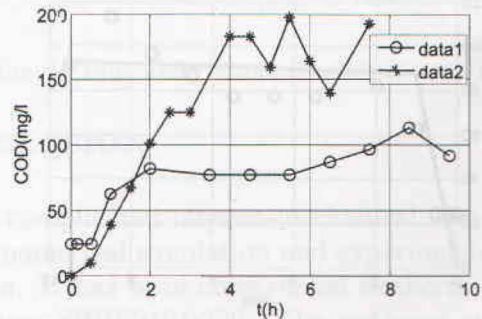


Fig. 4. Breakthrough curve of MinhKhai textile wastewater

In the Fig. 3 there is the result of kinetic experiment for textile wastewater. The value of solid diffusion coefficient is $1.31 \cdot 10^{-13} \text{ (m}^2/\text{s)}$. For textile wastewater, adsorbents

are very high molecular species, therefore they are affected strongly by pore's wall when flowing through it. It is the reason why D_s has very small value. It also proves that solid diffusion is the limited step of adsorption process (normally, the value of D_s varies from 10^{-8} to 10^{-12} m^2/s [8]).

3.2.3 Experimental result for constructing breakthrough curve

Textile wastewater is pretreated by coagulation method (using $Al_2(SO_4)_3$ with coagulant add, polymer A101). Experimental parameters are listed in Table 2 (case 1 and 2 correspond to data1 and 2 in Fig. 4, respectively). In both cases, experimental data show that, at output, COD increases fast in initial period. After that it increases slowly and is nearly parallel with horizontal axis.

4. NUMERICAL SIMULATION AND EXPERIMENTAL RESULT COMPARISON

4.1. Input parameters of mathematical model

Table 2. Input parameters for mathematical model

Parameter	Case 1*	Case 2*
COD_0 (mg/l)	207.23	346.98
ρ (g/l)	550	550
ε	0.475	0.475
d (dm)	0.009	0.009
v (dm/h)	160	135
H (dm)	2.6	2.45
t (h)	9.5	7.5
q^*	$2.5 \cdot 10^{-9} C^{5.22}$	$1.5 \cdot 10^{-9} C^{4.75}$
D_s (dm^2/h)	$4.716 \cdot 10^{-8}$	$4.716 \cdot 10^{-8}$

where, COD_0 is COD of influent (mg/l).

Input parameters for mathematical model presented by equation (2.1) and (2.2) are given in Table 2

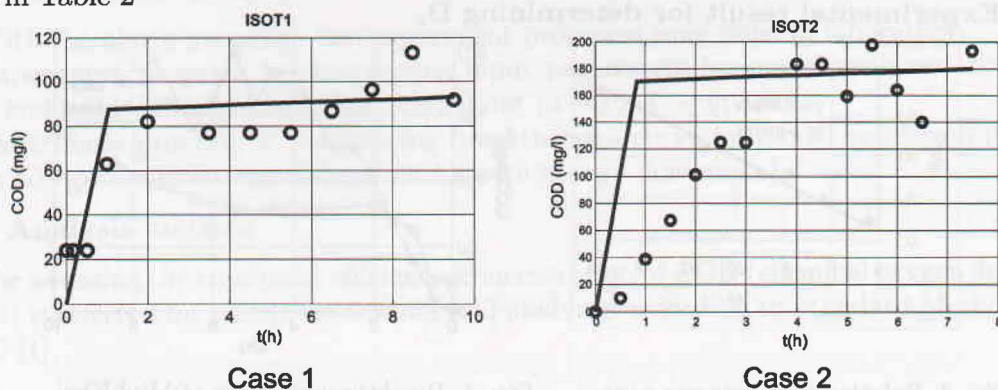


Fig. 5. Temporal COD variation at output of fixed bed column (empty point is experimental data and continuous line is model result)

4.2 Numerical Simulation results and comparison

COD behavior by the time at out put of column is shown in fig.5. With the input parameters shown in Table 2 (case 1 and 2), model results show that, NADPF model can be used to predict adsorption process in fixed bed column (Fig. 5).

Distribution of COD concentration in both liquid and solid phase shows that activated carbon has poor adsorbility with textile wastewater (Fig. 6 and 7). These results suit the isotherm curve (adsorption process is unfavorable).

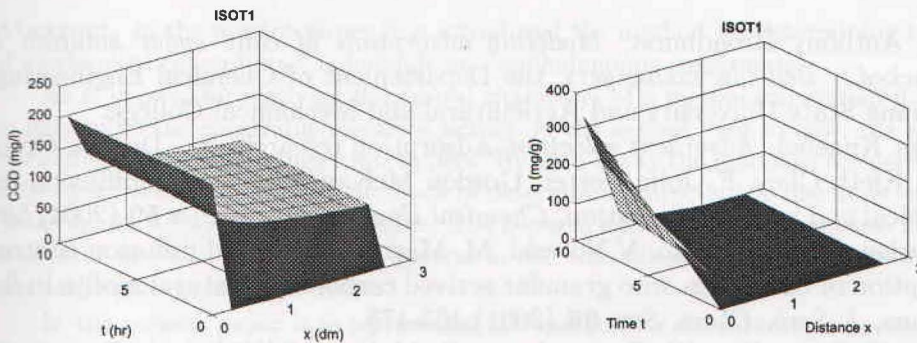


Fig. 6. Distribution of COD concentration in time and column length (Case 1)

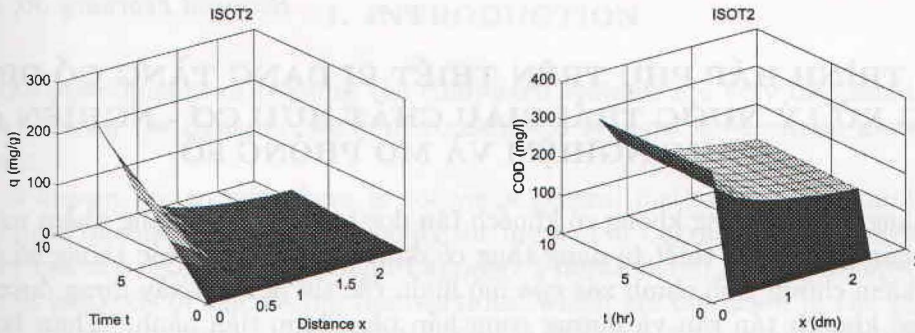


Fig. 7. Distribution of COD concentration in time and column length (Case 2)

5. CONCLUSION

Treating a rich organic wastewater is a complicated physico-mechanical problem. In this paper it is presented the first result in numerical simulation and experimental study of adsorption process on a fixed bed column. It has been constructed isotherm curve of textile wastewater with activated carbon type SWW210&220. The isotherm curve has been expressed by Freundlich equation. The solid diffusion coefficient of COD has been determined. None axially dispersed plug flow model (NADPF) can be applied to simulate adsorption process on a fixed bed column

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QUÁ TRÌNH HẤP PHỤ TRÊN THIẾT BỊ DẠNG TẦNG CỐ ĐỊNH TRONG XỬ LÝ NƯỚC THẢI GIÀU CHẤT HỮU CƠ - NGHIÊN CỨU THỰC NGHIỆM VÀ MÔ PHỎNG SỐ

Mô hình dạng đầy lý tưởng không có khuếch tán dọc trục được sử dụng nhằm mô phỏng quá trình hấp phụ trong thiết bị dạng tầng cố định. Để xác định các thông số đầu vào cũng như kiểm chứng tính chính xác của mô hình, các thí nghiệm xây dựng đường đẳng nhiệt, hệ số khuếch tán rắn và đường cong hấp phụ được tiến hành. Than hoạt tính SWW210 & 220 là vật liệu hấp phụ chính được sử dụng trong quá trình nghiên cứu. Mẫu nước sử dụng cho quá trình thực nghiệm là nước thải nhà máy dệt Minh Khai. Thông qua phương trình đường đẳng nhiệt hấp phụ, nước thải dệt nhuộm ít được hấp phụ trên than SWW210 & 220. Các số liệu về động học cho thấy giai đoạn khuếch tán của nước thải dệt nhuộm rất chậm ($D_s 1.31 \cdot 10^{-13} \text{ m}^2/\text{s}$). Đối với nước thải dệt nhuộm, mô hình NADPF có thể được sử dụng để mô phỏng quá trình hấp phụ.