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Modelling the Dynamic Adsorption of Methyl Violet from Aqueous Solution by *Posidonia oceanica* (L.) Dead Leaves

Posidonia oceanica (L.) Ölü Yaprakları ile Metil Morunun Sulu Çözeltiden Dinamik Adsorpsiyonunun Modellenmesi

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Abstract

There are some endemic species which are considered to have vital importance for aquatic habitats in the Mediterranean Sea. One of these species is *Posidonia oceanica* (Linnaeus) Delile. Since this species return to aquatic environment from the land in its evolutionary history, it protects its terrestrial plant characteristics and therefore the *P. oceanica* leaves are shed seasonally. Unfortunately, the dead leaves accumulated on the beaches are burned in order to cope with this aesthetic problem. It has been suggested in the current study that the accumulated material could be used as an alternative sorbent for the dynamic removal of methyl violet in a fixed bed column system instead of being burned. Column studies were carried out at different bed height and different flow rates. The conditions consisted of 9 cm bed height and 5 mL/min flow rate was detected as the optimum conditions for methyl violet removal. Column performance was evaluated by using Thomas and Bed Depth Service Time Models. The parameters related to these models were calculated and compared to experimental data. As a result of promising adsorption capacities of this accumulated material, it might be a cost efficient adsorbent for the treatment of textile industry's effluents.

Keywords: *BDST model, fixed bed column, methyl violet, Posidonia oceanica, Thomas model.*

Öz

Akdeniz'deki sucul habitatlar için hayati öneme sahip olduğu düşünülen bazı endemik türler vardır. Bu türlerden biri *Posidonia oceanica* (Linnaeus) Delile'dir. Bu tür, evrimsel tarihinde karadan su ortamına döndüğü için karasal bitki özelliklerini korur ve bu nedenle *P. oceanica*'nın yaprakları mevsimsel olarak dökülür. Ne yazık ki, bu estetik sorunla başa çıkabilmek için plajlarda biriken ölü yapraklar yakılırlar. Bu çalışmada biriken malzemenin, yakılmak yerine metil morunun sabit yataklı kolon sisteminde dinamik adsorpsiyonu için alternatif adsorban olarak kullanılabileceği önerilmiştir. Kolon deneyleri, farklı yatak yükseklikleri ve farklı akış hızlarında gerçekleştirilmiştir. 9 cm yatak yüksekliği ve 5 mL/dak akış hızından oluşan koşullar, metil morunun uzaklaştırılması için en uygun koşullar olarak tespit edilmiştir. Kolon performansı, Thomas ve Yatak Derinliği Servis Süresi

Modelleri kullanılarak değerlendirilmiştir. Bu modellerle ilişkili parametreler hesaplanmış ve deneysel verilerle karşılaştırılmıştır. Bu biriken malzemenin ümit vadeden adsorpsiyon kapasitesinin bir sonucu olarak, bu malzeme; tekstil endüstrisi atık sularının arıtılması için düşük maliyetli bir adsorban olabilir.

Anahtar Kelimeler: *BDST modeli, sabit yataklı kolon, metil moru, Posidonia oceanica, Thomas modeli.*

1. Introduction

The increase of the population of the world has brought out some problems such as limited food, water and etc. One of the solutions proposed to overcome of these problems is to development in industrial field. Although industrial development is a necessity to live comfortably, it can cause a lot of problems if the required precautions are not taken. Untreated effluents of industrial foundations are the major problem for environment, and especially for freshwater, all over the world. The industrial effluents generally include organic materials, heavy metals and dyes; therefore they can cause several health problems [1]. Among these pollutants, dyes are more stable against to degrade as a result of its complex molecular structure [2]. Therefore, scientists and environmentalists are increasingly emphasizing the importance of the dye removal from industrial wastewater prior to pouring it into natural water bodies as they can cause a lot of serious problems such as inhibiting photosynthetic activity by preventing sunlight penetration or producing toxic, mutagenic or carcinogenic effects on aquatic organisms by degrading partially and etc [3-6]. Various methods such as precipitation, chemical oxidation, photolysis, adsorption, and biodegradation have been used in order to cope with this problem [6,7]. Since the adsorption is the simplest and cheapest technique among them, it can be easily adapted to industrial applications. Besides, this method supply the advantages of not producing toxic substances [8] and reusability of adsorbents via regeneration [9]. The use of activated carbon is widely recommended in industry as an adsorbent due to its high specific surface area. Although it is suitable for wastewater treatment application, it has some limitations such as high cost and laborious regeneration procedures which restricts its usage in large scale [3]. Thus, scientists are doing more efforts to find cheap and easily available natural adsorbents for waste water treatment, nowadays. Various kinds of natural biological materials such as fruit peels, [10], plant leaves [11], maiza cob [12], various *Caulerpa* species [13-16], *P. oceanica* [5,17,18] and agricultural waste biomass such as pinus bark powder [19], tomato root [20], deoiled soya [9] have been used as adsorbents. Not only its low cost but also the important functional groups on the surface that contribute its higher adsorption capacity make the use of biomass in adsorption processes more advantageous than others. [5].

In this research, methyl violet (MV) adsorption onto *P. oceanica* dead leaves in a fixed bed column was investigated. It is known that the batch adsorption experiment results are generally inapplicable to most of industrial applications, but it gives some useful information such as optimum conditions for maximum adsorption, initial dye concentration, maximum adsorption capacity of used adsorbent, etc [1]. The maximum adsorption capacity of *P. oceanica* dead leaves was found as 119.05 mg/g in our previous study[5]. In order to present the applicability of the naturally accumulated waste material in industry, the fixed bed column studies were conducted with methyl violet due to its widespread use in textile industry, coloring papers, biological stain, veterinary medicine, dermatological material etc [21,22]. This research investigates the optimum design parameters of fixed bed column filled with *P. oceanica* powder for industrial applications. Different experimental conditions for flow rate and bed height were used for evaluating the column performance.

2. Material and Method

2.1. Adsorbent preparation and characterization

The *P. oceanica* dead leaves were collected from the Urla/IZMIR beaches in February 2010. After cleaning it as previously described [5], it was dried for 16 hours at 70 °C. The resulting material was milled to a particle size of 500 μm and then used for column studies.

Since the functional groups of any material have vital importance in sorption processes, FT-IR analysis of dried *P. oceanica* were conducted as previously described [5]. The peaks of the spectrum displayed that the main functional groups on the surface of ground *P. oceanica* (GPO) were hydroxyl (3200-3600 cm^{-1}), carboxyl (2800-3000 cm^{-1}), amine (3200-3600 cm^{-1}), carbonyl (1580-1700 cm^{-1}), sulfonyl (1000-1150 cm^{-1}), C-O (1000-1150 cm^{-1}) and S-O (500-650 cm^{-1}).

2.2. Adsorption studies in column and data analysis

Prior to the fixed bed adsorption experiments, the glass column (70 cm height and 1.2 cm internal diameter) was filled with GPO and the flux in the column was provided from up to down. The bed height effect on column performance was evaluated by using 0.25, 0.5 and 1.0 g of GPO that corresponds respectively the 2.7 cm, 4.8 cm and 9 cm bed height. Another parameter tested in terms of column performance is the flow rate and it was changed from 2 to 5 mL/min in experiments. The original concentration of MV was 100 mg/mL at the beginning of column experiments. The eluents after adsorption were collected in specified time intervals. MV concentrations in the effluents were determined at 585 nm in UV–vis spectrophotometer (Varian Carry 100). This column study was performed until no dyes were adsorbed by the adsorbent.

The performance of a column is generally evaluated by some parameters obtained from breakthrough curve. One of these parameters is the amount of total dye adsorbed in the column (q_{ad}) which can be computed from the plot of adsorbed dye versus time by using below equation [23]:

$$q_{ad} = \frac{F.A}{1000} = \frac{F}{1000}\int_{t=0}^{t=t_{total}} C_{ad}dt \qquad (1)$$

The difference between the original dye concentration and the waste dye concentration is represented by C_{ad}, the flow rate of dye is represented by F and finally the area under C_{ad} vs. t curve is represented by A. The uptake capacity (Q, mg/g) of the adsorbent can be determined via dividing the amount of adsorbed dye by the adsorbent mass (M) [24]:

$$Q = \frac{q_{ad}}{M} \qquad (2)$$

The breakthrough time (t_b) where dye concentration in the effluent reached 1 mg/L and exhausting time (t_e) where dye concentration in the effluent exceeded 99 mg/L are used to evaluate the breakthrough curves. Other column parameters known as overall adsorption zone (Δt) and length of mass transfer zone (Z_m) can be calculated by using Equation 3 and 4, respectively.

$$\Delta t = t_e - t_b \qquad (3)$$

$$Z_m = Z.\left(1 - \left(\frac{t_b}{t_e}\right)\right) \qquad (4)$$

where the depth of the bed in column (cm) is represented by Z.

Effluent volume (V_{eff}) can be found as follows:

$$V_{eff} = F.t_e \qquad (5)$$

where F is the flow rate (mL/min).

Total amount of dye (q_{total}) sent to the column can be determined by the Equation 6 [23]:

$$q_{total} = \frac{C_0.F.t_{total}}{1000} \qquad (6)$$

The percentage of total dye removal can be calculated as follows [24]:

$$Total\ removal\ \% = \frac{q_{ad}}{q_{total}}.100 \qquad (7)$$

The stoichiometric time (T_s) can be calculated in two different methods in accordance with the shape of breakthrough curves. While the time at which the effluent concentration reached to half of the initial concentration is denoted by T_s for symmetric curves, it can be calculated from the following equation for unsymmetrical curves [25]:

$$T_s = \frac{1}{C_0}\int_{t=0}^{t=t_e} C_{ad}dt \qquad (8)$$

2.3. Modeling of column experiments

In order to design column adsorption process successfully, the breakthrough curve of the system should have been analysed thoroughly. Although there have been many mathematical models for the evaluation of the performance of columns[26-29], two of them named Thomas Model and Bed Depth Service Time (BDST) Model were used to analyse the column experiments conducted in this study.

2.3.1. Thomas model

As a most widely used method in evaluating column performance, the Thomas model gives the opportunity to find adsorption rate constant and relationship between concentration and time [27]. The Thomas model can be expressed as below:

$$\frac{C}{C_0} = \frac{1}{1 + exp\left(\frac{k_{Th} Q_0 M}{F} - k_{Th} C_0 t\right)} \tag{9}$$

In order to calculate the parameters easily, this equation is arranged in the linearized form that is shown as follows:

$$ln\left(\frac{C_0}{C} - 1\right) = \frac{k_{Th} Q_0 M}{F} - k_{Th} C_0 t \tag{10}$$

where k_{Th} is the Thomas rate constant (mL/mg.min), Q_0 is the theoretical maximum solid-phase concentration of solute (mg/g) M is the mass of sorbent (g) and F is the flow rate (mL/min). The Thomas model parameters (k_{Th} and Q_0) can be calculated from the slope and intercept of the plot constructed with ln[(C_0/C)-1] vs t, respectively.

2.3.2. BDST model

The main purpose of the column adsorption system is to remove of adsorbate from the solution. Although this system works well at first, it loses its efficiency after some time. Therefore, determination of the time which the adsorbent material will not be able to remove adsorbate from solution before regeneration is the main problem in column systems. The period of time until regeneration is named the service time of bed [28].

Hutchins [30] showed that the service time of the bed depends to adsorption process parameters as shown below:

$$ln\left(\frac{C_0}{C} - 1\right) = \frac{k N_0 Z}{F} - \mathrm{k} C_0 t \tag{11}$$

where N_0 is the dynamic bed capacity (mg/L), k is the rate constant (L/mg.min) and F is the flow rate(cm/min) [31].

This equation is rearranged in order to determine the service time and this new version of the model is called BDST Model and expressed as follow [28,31]:

$$t = \frac{N_0}{C_0 F} Z - \frac{1}{C_0 k} ln\left(\frac{C_0}{C} - 1\right) \tag{12}$$

This model gives a simple approach for the prediction of column performance by presenting the relations between concentration and service time. This relation was firstly identified by Bohart and Adams [26] for the chlorine gas adsorption onto charcoal [26,31,32]. Although it was defined for gases originally, there have been many studies which presents this model can be used for other adsorption systems such as dye adsorption [32,33].

3. Results and Discussions

3.1. Determining the parameters of dynamic MV adsorption

The parameters such as the breakthrough time, the exhausting time, the total amount of dye adsorbed in the column, the uptake capacity, the percentage of total dye removal, etc for the evaluating of column performance were determined for the fixed bed adsorption of MV in different experimental conditions and the related results were presented in Table 1 and Table 2.

It can be clearly seen from the results that the lower flow rate was more favourable than the higher one for the removal of dye from the waste water. Similarly, the bed height can be the main parameter for column's performance if the flow rate is stable. A rise in bed height caused a rise in the total MV removal for the same flow rate conditions. The conditions consisted of 9 cm bed height and 5 mL/min flow rate was detected as the optimum conditions for MV removal.

Table 1. Various column parameters obtained at different bed heights and flow rates for the adsorption of MV onto *P. oceanica* (L.) dead leaves (initial MV concentration: 100 mg/L).

Z (cm)	F (mL/min)	t_b (min)	t_e (min)	Δt (min)	T_s (min)	V_{eff} (L)	Z_m (cm)
2.7	2	76	468	392	296.02	0.94	2.26
2.7	3.5	36	288	252	202.84	1.01	2.36
2.7	5	28	220	192	150.92	1.06	2.34
4.8	5	68	432	364	298.78	2.10	4.02
9	5	312	768	456	643.71	3.84	5.34

Table 2. Various column parameters obtained at different bed heights and flow rates for the adsorption of MV onto *P. oceanica* (L.) dead leaves (initial MV concentration: 100 mg/L).

Bed height (cm)	Flow rate (mL/min)	Area (mg.min/L)	q_{ad} (mg)	q_{total} (mg)	Total Removal of MV (%)	Column Uptake Capacity, Q (mg/g)
2.7	2	29607	59.2	97.6	60.7	236.9
2.7	3.5	20286	71.0	102.2	69.5	284.0
2.7	5	15096	75.5	108	69.9	301.9
4.8	5	29881	149.4	212	70.5	298.8
9	5	64376	321.9	388	83.0	321.9

3.2. Bed height effect on column performance

The effect of bed height on the performance of fixed bed column were determined by using columns that contain different amounts of GPO. The breakthrough curves were plotted for the adsorption of MV onto GPO at various bed heights (2.7 cm, 4.8 cm, 9 cm) and a constant flow rate of 5 mL/min. The results were presented in Figure 1.

The breakthrough times were found to be 28 min, 68 min and 312 min for the columns having 2.7, 4.8, 9 cm bed heights, respectively. The results also indicated that the uptake capacity of the column increased with increasing bed heights. The total MV removal percentages were found to be 69.9%, 70.5% and 83.0% at bed heights of 2.7, 4.8, 9 cm, respectively.

A possible cause of the observed results may be the presence higher amount of adsorption sites in the higher amount of GPO. Some of the previous scientific literature also contained similar results with ours [18,31,34]. In addition to this, the increase in the bed height of the column induces an increase in the residence time of the dye inside the column which contributes the higher diffusion of dye molecules into the adsorbent [28,34]. Thus, the total removal percentage of the column can be changed with the effect of bed height.

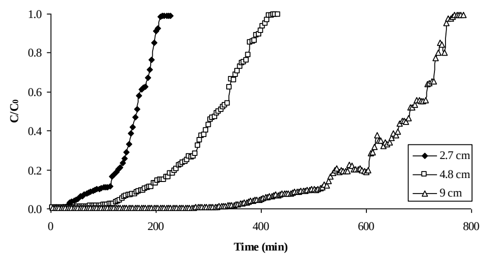

Figure 1. Breakthrough curves for the adsorption of MV onto *P. oceanica* (L.) dead leaves at different bed heights and F=5 mL/min.

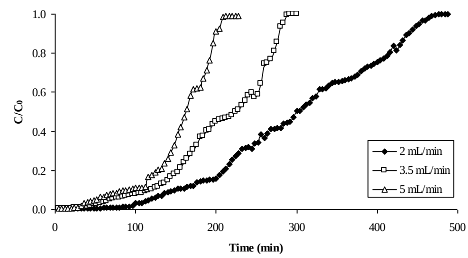

Figure 2. Breakthrough curves for removal of MV by *P. oceanica* (L.) dead leaves in fixed bed column at different flow rates and Z=2.7 cm.

3.3. Flow rate effect on column performance

The effect of flow rate on the column performance was detected via conducting column experiments with different flow rates (2 mL/min, 3.5 mL/min, 5 mL/min) at a constant bed height (Z=2.7 cm) and the results were shown in Figure 2.

Figure 2 showed that the breakthrough curve became steeper, while the flow rate increased from 2 to 5 mL/min as higher flow rates represent the lower contact time between the dye and the adsorbent. As a result of lower interaction between the dye and the adsorbent, the adsorption equilibrium cannot be occurred and the dye leaves from the column. In this instance the adsorbent becomes less saturated due to a lower contact time. Similar results were also reported in the literature by some researchers [28,31,34,35]. Figure 2 also revealed that an increase in flow rate leads to a shift to an earlier time in breakthrough and exhaustion times. Besides all these findings, it can be obviously seen from the Figure 2 that the service time of the bed decreased with increasing flow rate. As seen in Table 2, the column uptake capacity increased from 236.9 to 301.9 mg/g when the flow rate increased from 2 to 5 mL/min.

3.4. Application of Thomas and BDST models

In order to evaluate column parameters for industrial applications, the data obtained from experimental studies were applied to two different models. The curves which are related to Thomas model were shown in Figure 3 and their parameters were listed in Table 3.

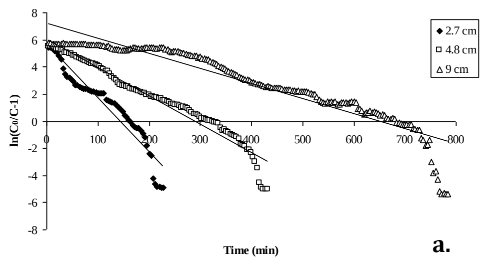

Figure 3. a. Plot of $\ln[(C_0/C)-1]$ vs. t representing removal of MV by *P. oceanica* (L.) dead leaves in fixed bed column according to Thomas model at different bed heights and F=5 mL/min.

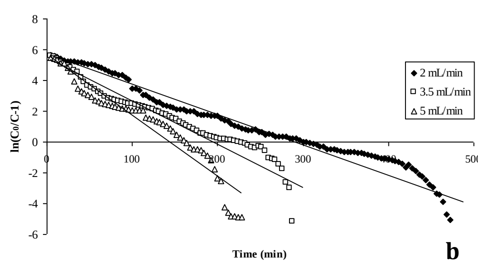

Figure 3. b. Plot of $\ln[(C_0/C)-1]$ vs. t representing removal of MV by *P. oceanica* (L.) dead leaves in fixed bed column according to Thomas model at different flow rates and Z=2.7 cm.

Table 3 showed that an increase in the flow rate at fixed bed height caused an increase in Thomas rate constant which represents a decrease in the mass transport resistance [36,37]. In contrast to this, the constant decreased with increasing bed height at fixed flow rate. Besides, the theoretical maximum adsorption capacities of GPO column for MV were very close to their corresponding experimental ones. This similarity between the theoretical and experimental results revealed that Thomas model can be used to characterize the MV adsorption onto GPO in fixed bed system. The increase in adsorption capacity with increasing bed height may have probably been caused by the increased contact time between MV and GPO.

Table 3. Thomas model parameters for the adsorption of MV onto *P. oceanica* (L.) dead leaves at different bed heights and flow rates.

Z (cm)	F (mL/min)	k_{Th} (x10^{-4} L/mg.min)	Q_0 (mg/g)	R^2
2.7	2	1.83	240.2	0.962
2.7	3.5	2.57	285.5	0.927
2.7	5	3.77	294.8	0.916
4.8	5	2.06	292.7	0.960
9	5	1.04	338.9	0.913

In our previous study in which we determined the basic parameters of MV adsorption onto GPO in batch system, the pseudo second-order model and Langmuir isotherm model was found to correspond well with the experimental results [5]. Thus, it is expected that the Thomas model would be a good model for describing the fixed bed adsorption of MV onto GPO, since the Thomas model well describes the adsorption processes based on the Langmuir isotherm for equilibrium and second-order reaction kinetics [3,8,37,38]. Since the second-order kinetics specifies the chemisorption process, it can be regarded that the adsorption of MV onto GPO stems from the interaction between the functional groups of MV and GPO. Indeed, the positively charged dye molecules might have bounded with the negatively or partially negatively charged areas of the adsorbents such as –OH, –C = O, and –NH group-bounded areas. Similar results have already been reported in the scientific literature [5,13,39].

The other model used for the evaluating of the efficiency of column is the BDST model which provides a simple approach for evaluating the relationship between bed height and service time [34,37]. Results of varying the bed height from 2.7 cm to 9.0 cm experiments with a constant flow rate of 5 mL/min were evaluated with BDST equation (Figure 4). The dynamic bed capacity and adsorption rate constant were calculated as 42.99 mg/L and 0.113 L/mg.min, respectively. The critical bed depth (Z_o) which implies the minimum required value of adsorbent sufficient not to exceed the breakthrough concentration at t=0 was found to be 4.75 cm.

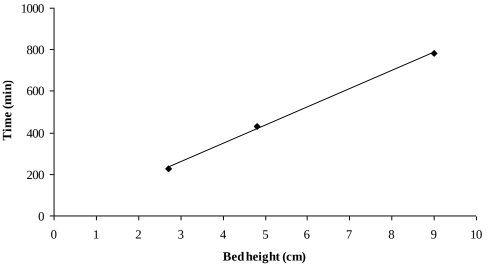

Figure 4. BDST model plot for removal of MV by *P. oceanica* (L.) dead leaves in fixed bed column (F=5 mL/min).

Table 4 shows the comparison between the results of this study and the results of previously reported scientific studies that used various biosorbents for MV removal in the literature.

4. Conclusion

The present paper suggests an alternative approach for the evaluation of waste biomass, dead leaves of *P. oceanica*, instead of burning it since it contains many functional groups. Many of the industrial firms use activated carbon to get rid of their waste waters. Although activated carbon provides good results to clean the industrial effluents, it has a cost disadvantage. Due to this fact, especially in recent years, scientists make a great efforts in order to find cheap and easily available natural adsorbents for industrial applications. This paper shows that the *P. oceanica* dead leaves can be a promising cost efficient material for the treatment of textile industry's effluents. Although P. oceanica was used as an alternative material in the study, we never suggest collecting of the alive P. oceanica under the water because of its vital importance for the Mediterranean Sea, as we reported in our previous paper.

Table 4. Maximum adsorption capacities of various biosorbents for methyl violet

Biosorbent	Temperature (°C)	q_{max} (mg/g)	References
Banana peel	30	12.20	[10]
Orange peel	30	11.50	[10]
Calotropis procera leaf	-	4.14	[40]
Coniferous pinus bark powder	30	32.78	[19]
Tomato plant root	-	94.34	[20]
Bottom ash	30	4	[9]
Deoiled soya	30	5.14	[9]
Grapefruit peel	-	249.68	[6]
Treated ginger waste	50	277.77	[22]
GPO	45	109.05	[5]
GPO	25	321.9	This study

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