Journal of Alasmarya University: Basic and Applied Sciences
Vol. 6, No. 5, December 2021, Special Issue for Forth Conference on Engineering Science and Technology (CEST-2021)
مجلة الجامعة الأسمرية: العلوم الأساسية والتطبيقية
المجلد 6 ،العدد 5، ديسمبر 2021، عدد خاص بالمؤتمر الرابع للعلوم الهندسية والتقنية (CEST-2021)

MECHANISM AND KINETIC STUDIES OF METHYLENE BLUE ADSORPTION ON COMMERCIAL POLYURETHANE FOAM

Abdelsalam Asweisi[1], Khalifa Algheryani[2,*]

[1]*Chemical Engineering Department, Faculty of Engineering, University of Tripoli, Tripoli, Libya,* a.amhmed@uot.edu.ly,

[2]*Chemical Engineering Department, Faculty of Engineering, University of Tripoli, Tripoli, Libya,* k.algheryani@uot.edu.ly

ABSTRACT

Separation of several organic dyes and trace elements from aqueous effluents have a great importance in many areas of research today. Therefore, the main objective of this work was to remove methylene blue (MB) dye from effluents by using cost effective and environmentally method like adsorption. To achieve this work, batch experiments were carried out with an artificial effluent comprising of MB dye in deionised water. The effects of the initial dye concentration, volume, PH value, stability and removal kinetics were studied. An adsorbent dosage of 0.5 g/L was effective in height removal percent of the dye ion, at pH 12.6, and equilibrium time 20-25 minutes. Also, the kinetic process of MB adsorption onto polyurethane foam (PUF) was investigated by applying Lagergen pseudo-first-order and Morris-Weber models to correlate the experimental data and to estimate the kinetic parameters. The adsorption isotherm data were correlated by the Langmuir and Freundlich models. A maximum monolayer adsorption capacity of 0.0929 mg/g was calculated using the Langmuir adsorption isotherm, suggesting a functional group limited adsorption process. The results confirmed that foam are effective sorbent for the removal of dye from effluent.

Keywords
Methylene blue.
Polyurethane foam.
Adsorption isotherms.
Kinetic models.

*Corresponding Author Email: k.algheryani@uot.edu.ly

1 INTRODUCTION

The ability to separate organic dyes and trace elements in various types of samples is important in many areas of research including food, pharmaceutical, agriculture, forensic and environmental science. There are three types of organic dyes, acidic, basic and uncharged dyes. Basic dyes are used for modified polyesters, modified nylons, polyacrylonitrile dyeing as well as in paper industry and medicines. These are also used for tannin mordant cotton, silk and wool [1, 2]. This class of dyes is soluble in water and yields coloured cations and are also called cationic dyes [3]. The major classes are cyanine, thiazine, acridine, oxazine, hemi cyanine and diazahemicyanine, i.e., basic red 46, malachite green, basic yellow 28, crystal violet and methylene blue.

Discharging of some dyes shush as MB into natural water bodies prior to treatment could contribute to water pollution because of their persistence and non-biodegradable characteristics [4]. Highly concentration can cause some specific harmful effects in humans such as vomiting, heartbeat increase, cyanosis, shocks, jaundice and tissue necrosis as well as it can affect aquatic life found in natural water bodies by reducing sunlight penetration and/or even causing direct poisoning to living organisms [5,6]. In order to avoid these problems, effluents containing dyes must be treated for their removal before disposal.

Several solid materials have been recently used for the extraction and adsorption of dyes [6-8, 10,11] including methylene blue. Different experimental conditions were investigated.

Polyurethane foam has been widely used in many industries especially in furniture's during the last and recent centuries, the rest of the foam is usually remains as a chemical waste. During the past decades, polyurethane foam and many other solid materials have been tested as stationary phase for extractions of large numbers of toxic organic and metal ions from aqueous solutions and some organic solvents. PUF is able to retain different types of hazardous chemicals like organic dyes because of the presence of polar and nonpolar groups in their structures [12] The large surface area and cellular structures of polyurethane foam gives the possibilities of using the foam as columns filling materials for solid phase extraction and pre-concentration have been studied [12]. The interesting of this material has increased as sorbent material for air and gaseous samples by passing it through backed column or tube to extract organic vapours or other substances present in the sample [13].

Adsorption on polyurethane foam is very effective in reducing cost as compared with other on different solid phases using clay sorbent (Bentonite – 0.05–0.2; Red mud 0.025; Clinoptilolite – 0.14–0.29) U$/kg, commercial active carbon (0.8–1.1 U$/kg), natural zeolite (0.08 U$/kg), Chitin (15–20 U$/kg), Chitosan (16.5–10 U$/kg) Cross-linked-chitosan (5–10 U$/kg) [8,9]. (KOSAR).

This work is aimed to study and develop the adsorption process of MB dye on PUF and to describe the mechanism of adsorption and kinetic behaviour of the process. To study the possibilities of using MB loaded PUF as sorbent material for trace elements and for other organic molecules.

2 MATERIALS AND METHODS

All chemicals and reagents were of analytical grade. High purity water was used throughout.

2.1 Apparatus.

The absorption measurements were made using UV-VIS spectrophotometer JENWAY. The PH measurement were made by JENWAY 3150 PH-METER.

2.2 Preparation of dye solution.

A stock solution was prepared (100ppm) by dissolving 0.1g of MB in one litter of distilled water. MB solutions of the desired concentrations 2,5,8, and 10 ppm were prepared from the stock solution by appropriate dilutions with distilled water.

2.3 Preparation of absorbent material.

The sample of foam was obtained from Al-Khums sponge factory (Northwest Libya) and it has been washed many times with 2M of HCl solution then rinsed with water and dried. Loaded polyurethane foam was prepared by immersing certain amount of foam in 100 ppm dye solution and left for one week then dried.

3 RESULTS AND DISCUSSION

3.1 Stability of methylene blue solution.

Aqueous solution of methylene blue is relatively unstable and it undergoes photodegrading with time, the decrease in absorption of methylene blue solution after one week time is shown on calibration curves in figure 1. About 10% decrease in concentration of methylene blue solution at concentration of 6.0 ppm is observed. Lower concentrations up to 2.0 ppm shown lower percent of photodegradation. The calibration curves were with R^2 = 0.998 and 0.987 for one week old and freshly prepared methylene blue solution respectively.

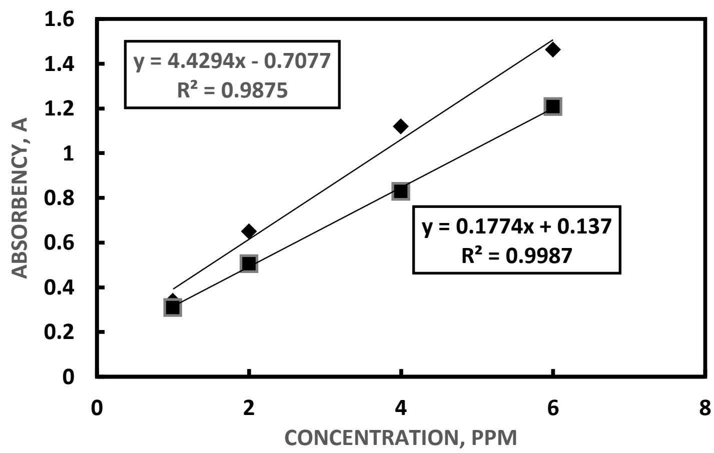

Figure 1. Calibration curves of fresh and after one week.

3.2 Effect of pH.

Effect of pH value in the adsorption process plays an essential role in order to increase/decrease separation efficiency, especially on the adsorption capacity, due to its influence on the surface properties of the adsorbent and ionic forms of the MB solutions. In this work, the effect of pH on the methylene blue uptake was investigated by batch procedure. An aliquot of 2.0 ppm solution of dye at varying pH values ranging from 7.09, 9.25, 11.1, and

12.6 was stirred with 0.50 g foam for different time intervals. The results obtained are shown in figure 2.

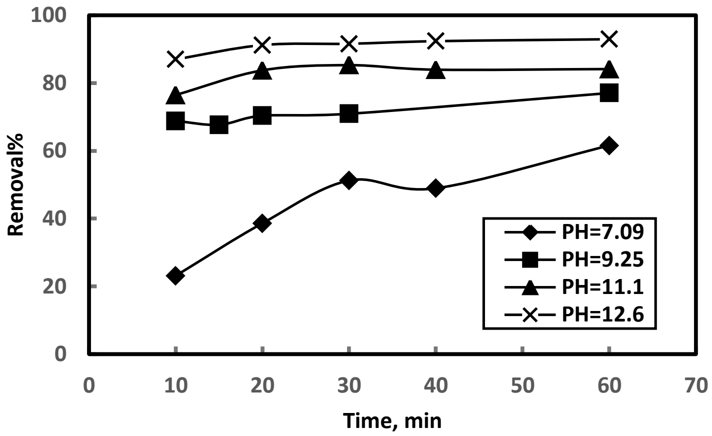

Figure 2. Effect of PH on methylene blue adsorption at different times.

It was found that the dye uptake increased at higher pH values from 9.5 and above and equilibrium reached after 10.0 min, while at lower pH values the percent removal become less and more time needed to reach equilibrium. The possible explanation for higher adsorption in the alkaline region refers to the increasing negatively charged active sites or in other words, the excess negative ions (OH^-) formed in methylene blue solution was bonded with the positive ions (S^{++}) of the dye and left the medium to adsorb on the absorbent surface according to the next equation:

$$MB: S^{++} + xOH \rightarrow MB: S^{++}(OH)_x(s), \quad (1)$$

The best sorption condition is at pH =13 and equilibration time of 20-25 min.

3.3 Effect of sample volume.

The effect of sample volume on adsorption process and percent removal was studied using 2.0 ppm of MB solution at different times. It’s clearly noticed that, figure 3, the increase in sample volume generally decreases the surface area of the adsorbent which lead to decrease the percent removal of the MB ion in dye solution from about 95% for 20.0 mL sample volume to 88 % at 100 mL and vice versa.

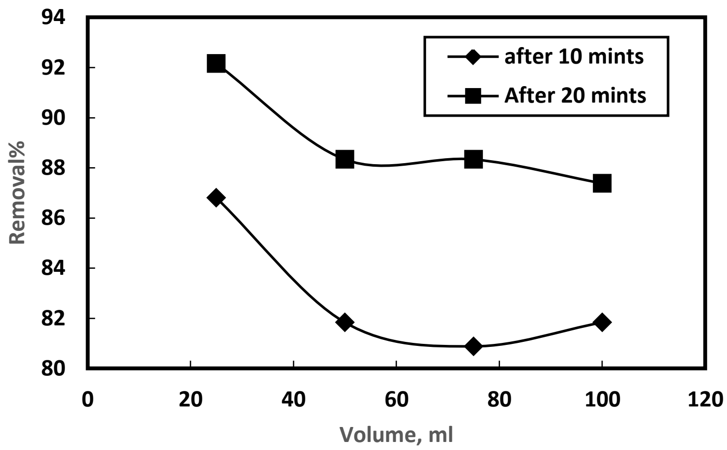

Figure3. Effect of sample volume on percent removal of dye.

3.4 Isotherm studies.

Dye uptake was estimated from mass balance based on initial and final dye concentrations in the original and final solution [14]:

$$q(mg/g) = \frac{[C_0 - C_t](mg/L)}{m(g)} V(L), \quad (2)$$

Where q is the dye uptake; C_0 and C are the initial and final dye concentration in solution. m is the mass of sorbent and V is the volume of solution used**.**

3.4.1 Langmuir isotherm model.

The Langmuir adsorption isotherm model is used to describe the equilibrium between adsorbate and adsorbent system [14] and is expressed as:

$$q_e = \frac{q_m b C_e}{1 + bC_e}, \quad (3)$$

A linear form

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}, \quad (4)$$

where q_e (mg/g) and C_e (mg/L) refer to the amount of adsorbed dye per unit weight of adsorbent and unabsorbed dye concentration in solution at equilibrium, respectively. q_m and b are Langmuir equilibrium constants related to the sorption capacity and the apparent energy of sorption, respectively. The values of q_m and b for adsorption of MB dye on PUF sorbent were estimated from the slope and intercept of the linear plot of C_e/q_e versus C_e.

The equilibrium parameter or separation factor (R_L) whish represents the essential characteristics of the Langmuir isotherm relation was estimated from equation (5):

$$R_L = \frac{1}{1 + bC_0}, \quad (5)$$

The value of R_L indicates the type of sorption isotherm to be linear ($R_L = 1$), favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), and irreversible ($R_L = 1$). It can be noted that for this work, R_L is negative value, which indicates sorption of MB by PUF.

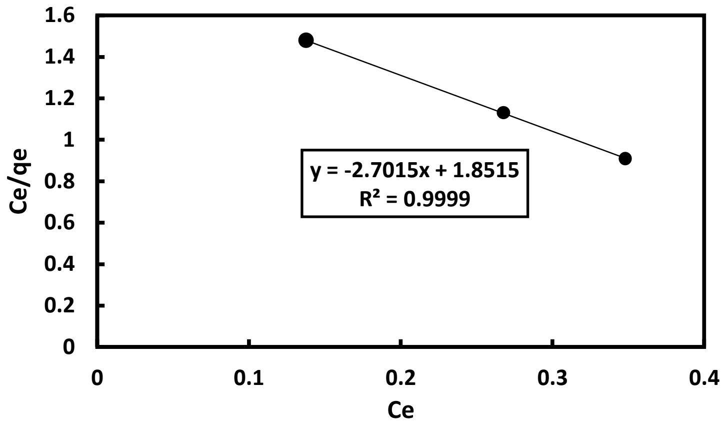

Figure 4. Langmuir adsorption isotherm for MB dye on PUF.

3.4.2 Freundlich isotherm model.

This model is often used for the study of the sorption behaviour of heterogeneous surface energy systems [14] and is expressed as

$$q_e = k_f C_e^{1/n}, \quad (6)$$

A linear form

$$\log q_e = \log K_f + \frac{1}{n} \log C_e, \quad (7)$$

Where q_e (mg/g) represents the amount of dye adsorbed; C_e (mg/L) is the dye concentration at equilibrium; K_f and n are empirical constants which indicate to the adsorption capacity and intensity, respectively, and can be determined graphically from the linear plot of $\log q_e$ versus $\log C_e$. Acordingl, the adsorption of dye on foam was tested by using Freundlich isotherm. The investigation showed linear relation between adsorbed amount and dye concentration. Monolayer adsorption could be clear from the value of Freundlich constant (n = 0.67). the results obtained are shown below in Figure 5.

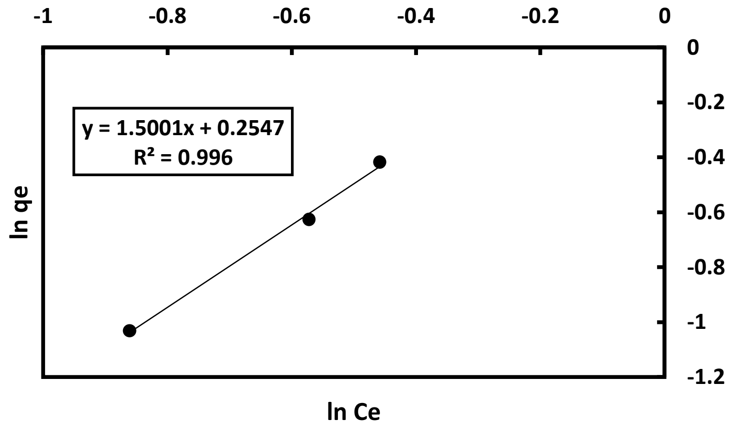

Figure 5. Freundlich adsorption isotherm of MB on PUF.

3.5 Kinetic studies.

The adsorption process of the dye depends on the effective collisions between the polyurethane foam as a solid-phase and the molecules of the dye in solution. Collision of molecules could be increased by shaking of solution. A certain time is required for foam- dye interaction to reach equilibrium and to achieve maximum adsorption of dye on foam. The polyurethane foam is highly porous material with spherical and symmetrical macro and micropores. The micropores are relatively small as compared with the larger molecule of dye. Sorption of dye molecules will less than that if compared with smaller particles such as metal ions in solution, diffusion mechanism is unfavourable for dye molecules into foam micropores.

3.5.1 Lagergen model.

This model was applied for mass action phenomenon and which is given by [14]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \quad (8)$$

After integration and simplification, a linear form is

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}, \quad (9)$$

Where q_e and q_t (mg/g) represent the amount of adsorbed dye on PUF at equilibrium and any time t, k_1 $(1/min)$ is the Lagrange kinetic rate constant first-order which determined graphically from the linear plot of $\log(q_e - q_t)$ versus $\log t$, figure 6.

The constant, $k_1 = -0.0284\ (1/min)$.

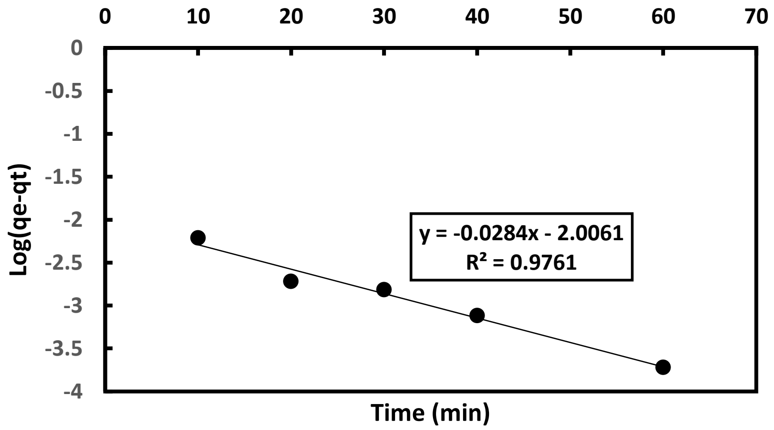

Figure 6. Lagergen plotting for adsorption of dye on foam.

3.5.2 **Morris-Weber equation.**

The adsorption behaviour of MB dye on PUF was tested by using Morris-Weber equation [15] in the form

$$q_t = k_i(t)^{1/2}, \quad (10)$$

Where qt is the amount of dye adsorbed at time t and k_i is the adsorption rate. The straight line of the plot q_t Vs t with R^2=1 indicates the intra particle transport phenomenon of dye into foam. In the diffusion process the slope of the curve depends on the particle size, film thickness and distribution coefficient of dye molecules where as in mass action, the rate depends on temperature and concentration of solute in solution. The plot of Morris-Weber equation is shown in figure 7. The constant $k_i = 0.5991$.

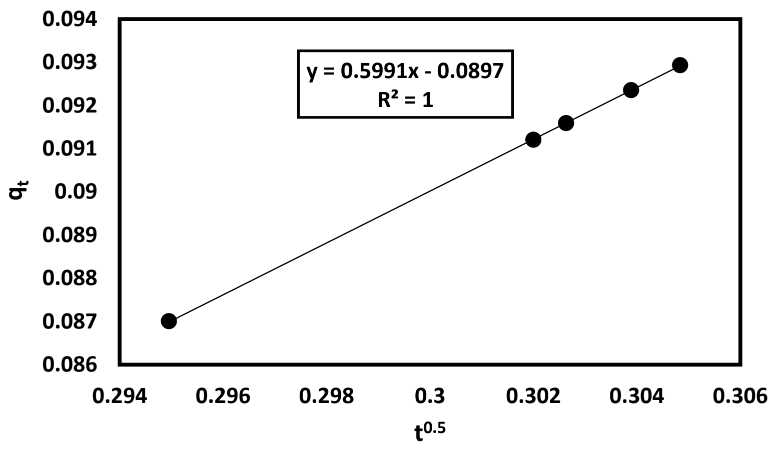

Figure 7. Plotting of Morris –Weber equation for dye- foam interaction.

Also, this study was extended to investigate the competitive effect of some metal ions and dyes which usually presented in effluents by the adsorption on the PUF, chlorophenol, murexide, methyl green, iron (II) and Mn (II) were. Iron showed very strong reduction for the dye solution and colour disappearance. The recovery of dye was reduced into lower values because of the presence of these species in solution. Loaded polyurethane foam the dye becomes more stable and no further reduction due to Iron ions. The results are shown if figure 8.

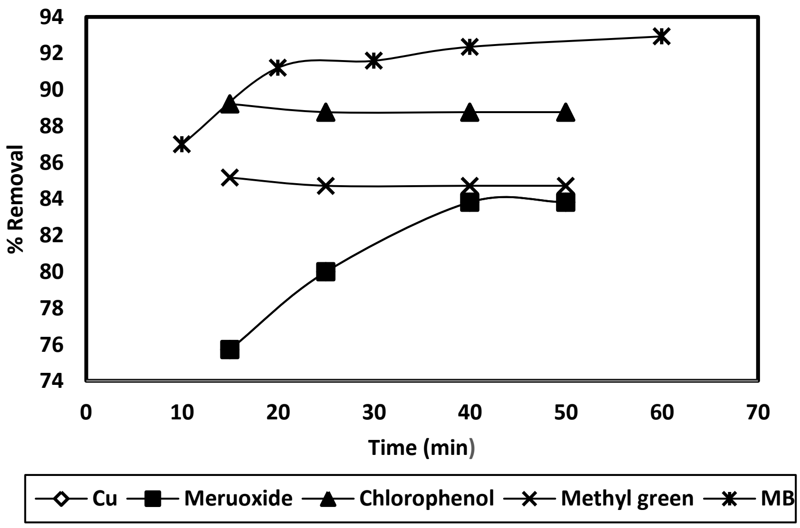

Figure 8. Competition effect of some species on dye adsorption.

4 CONCLUSIONS

It is possible to use the rest of polyurethane foam to removes some chemical wastes like methylene blue dye at certain conditions. The loaded foam could also be used for further separation. The results obtain were in good agreement with previous studies on adsorption of methylene blue on polyurethane foam. Absorption seems to be chemical with monolayer adsorption behaviour. Loaded and unloaded polyurethane follows pseudo first order kinetics model, the best adsorption condones could be achieved at pH =13 and stirring time of 15 min and above. Reverse reaction of releasing dye again into solution is very slow since dye stayed adsorbed on foam for more than two weeks.

ACKNOWLEDGMENT

We are gratefully acknowledgements to Chemical Eng. Department, University of Tripoli.

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دراسة آلية وحركية امتزاز صبغة الميثيلين الزرقاء على سطح البولي يوريثان التجاري

عبد السلام السويسي[1] ، خليفة الغرياني[2,*]

[1]قسم الهندسة الكيميائية ، كلية الهندسة، جامعة طرابلس ، طرابلس، ليبيا، a.amhmed@uot.edu.ly
[2]قسم الهندسة الكيميائية ، كلية الهندسة، جامعة طرابلس ، طرابلس، ليبيا، k.algheryani@uot.edu.ly

الملخص

فصل العديد من الأصباغ العضوية والعناصر المعدنية من النفايات السائلة له أهمية كبرى في مختلف المجالات الصناعية والبحثية. لذلك، فان الهدف الرئيسي من هذه الدراسة هو إزالة صبغة الميثيلين الزرقاء (MB) من النفايات السائلة باستخدام طريقة أكثر فعالية من حيث التكلفة والبيئة مثل الامتزاز. ولأجل تحقيق ذلك، تم إجراء سلسلة من تجارب الامدصاص على دفعات لدراسة تأثير معايير مهمة لإزالة الصبغة منها تأثير قيمة الأس الهيدروجيني (pH) ووقت التماس وتركيز المادة الممدصة و حجم المحلول وكذلك حركية الإزالة. من نتائج تجارب الامدصاص عند تفاعلات الاتزان يتضح أن كمية المادة المازة 0.5 جم/لتر كانت فعالة للحصول على أعلى نسبة إزالة لأيون الصبغة، عند الرقم الهيدروجيني 12.6، وزمن الاتزان 20-25 دقيقة. أيضا، تم دراسة حركية امدصاص أيونات صبغة MB على سطح البولي يوريثان التجاري (PUF) من خلال تطبيق نماذج الحركية من الدرجة الأولى وقد أظهرت النتائج تطابق نموذج Morris-Weber بشكل جيد مع النتائج المعملية أكثر من نموذج Lagergen. كما تم التحقق من بيانات ايزوثيرم الامتزاز باستحدام نموذج لانكماير وفرندليش. تم حساب القيمة العظمى للامدصاص وكانت 0.0929 مجم / جم باستخدام نموذج لانكماير، مما يشير إلى أن عملية الامدصاص عملية كيميائية أحادية الطبقة. كما أكدت النتائج أن PUF مادة ماصة فعالة لإزالة الصبغة من النفايات السائلة وبتكاليف منخفضة.

الكلمات الدالة:
أيزوثيرم الامتزاز.
البولي يوريثان التجاري.
الميثيلين الأزرق.
النماذج الحركية.

*البريد الإلكتروني للباحث المراسل: k.algheryani@uot.edu.ly