

Removal of Heavy Metal Ions Using Polystyrene Nanocomposite Thin Films

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POLYMER nanocomposite thin films consisting of polystyrene and furnace carbon black were prepared in this study as adsorbent materials for the removal of heavy metals from industrial wastewater. The film properties were characterized, and the effect of initial concentration, separation time, and pH on the removal efficiency was investigated. The optimal operating conditions were 120 min of separation time at pH 6 with 30 ppm of initial concentration. The adsorption equilibrium data and adsorption kinetics are also described herein. The Freundlich model best fit the equilibrium data, and the adsorption rate followed pseudo second-order kinetics.

Keywords: Removal, Polymer nanocomposite, Pollution, Thin film.

Introduction

Heavy metals are dangerous environmental contaminants and pose a threat to human health. As an example of the danger of heavy metals, the mercury contamination of Minamata city must be mentioned. This incident was one of the most significant environmental disasters, because of which mercury poisoning came to be known as the Minamata disease, signifying the risk that heavy metal contamination poses. The dangerousness of heavy metals comes from their tendency to accumulate[1], and various human activities can cause heavy metal pollution. The sources of heavy metals can be classified into five major categories: geochemical; agricultural impurities, pesticides, and metal corrosion; metallurgical industry from manufacturing and recycling of alloys; waste disposal from landfills and incinerators; and other manufacturing sources such as batteries and paints[1].

Scientists realized the issue of heavy metal contamination long ago and have focused their efforts on finding efficient methods to remove these pollutants and develop effective materials for this purpose. Coagulation, flotation, chemical oxidation, and adsorption are examples of techniques used for treating wastewater [2,3]. The adsorption of pollutants is preferable because it is efficient and can separate many chemicals simply and effectively [4]. Many research groups have focused on developing novel materials with

improved efficiency and acceptable cost, utilizing materials such as biomass [5-8], clay [9,10], waste materials, [3,11] and polymer nanocomposites [2,12].

The need to further develop materials for heavy metal removal is ongoing. Acceptable cost with efficient performance and the ease of operation are the most important parameters for any new adsorbents for commercial production. Therefore, polymer nanocomposite thin films are an attractive alternative to conventional materials.

In our previously published work [13], nanocomposite films of polystyrene and nanoparticles of furnace carbon black were prepared via simple mixing process and characterized spectroscopically, microscopically, electrically and mechanically. This work comes to be an applied study of it to examine their adsorbability and applicability for the removal of lead (Pb^{+2}) from a heavy metal-contaminated target under various operational conditions, such as the content filler in the composites, lead concentration, separation time, and pH were tested to determine the optimal operating conditions.

Experimental

Materials and preparation method of the film were reported in our previous study in details [13], with slight changes to the filler content to achieve the aims of this study.

Materials

Matrix: Polystyrene from Sabic Co. There are different grades produced of polystyrene by the company, and the used product was PS330.

Reinforcement: Furnace carbon black (FCB) from Degussa Co., and the data of this product as follows [13]:

pH is 7, ash content is 0.05%, volatiles is 1.0% and particle size is 95 nm.

Solvent: Toluene from BDH Co. was chosen because of it less toxic than the other solvent such as benzene, and completely dissolve the polystyrene without any clump of solid PS could be left behind, not as noted with the acetone solvent after evaporating. For environmental considerations, D- limonene is suggested as a natural solvent [14].

Methods

To prepare the film, preparative method as reported in our previous study [13] was followed. A suspension of FCB in 50 mL of the solvent was stirred magnetically for 1 h, and then 5 g of the polymer was added and stirred at 50 °C for further 60 min. Subsequently, the mixture was cast on a glass slide and left for the solvent to evaporate at ambient temperature. The ratio of the furnace carbon black to polymer was 15 wt% for the prepared films.

Several analyses were performed to characterize the properties of the film, including tensile testing using an Instron Corporation – Model 8500 materials instrument according to D882-02, and thermal stability using a Perkin-Elmer Thermal Analysis Systems-TGA 7 Thermogravimetric Analyzer at a heating rate of 10 °C/min from 25 °C to 600 °C under a nitrogen atmosphere, surface area was determined using a Nova analyzer (Quantachrome Instrument version 2.1) by measuring the BET and Langmuir adsorption isotherms for Nitrogen gas adsorption, and the morphology of the film surface before and after the removal process was analyzed using SEM (Quanta 250) to observe any changes could be obtained.

Lead removal studies were performed with various concentrations of lead ions. The experiments were performed by immersing a piece of the film with an area equal to 4 cm² into the lead ion solutions, followed by continuous agitation for a specific time. Subsequently, the film was removed, and the samples were analyzed using *Egypt.J.Chem.* 62, No. 1 (2019)

PC-controlled double-beam atomic spectroscopy (SavantAA GBC with GF 5000 Graphite Furnace, UK).

The conditions of the experiments were designed to study the influence of the following factors:

1. Initial concentration of lead ion solutions: This factor was investigated using a series of the lead solutions with concentrations equal to 5, 10, 15, 20, 30, 50ppm at constant conditions of pH 5, 120 min separation time, and at 25 °C.
2. Separation time: This factor was tested by performing the reaction for 15, 30, 60, 90, 120, and 180 min at fixed conditions of pH 5, 30 ppm lead solution, and at 25 °C.
3. pH: This factor was also investigated by adjusting the lead solution to a pH of 4, 5, 6, 7, 8, or 9 using a Hydrolab sensor (WTW Multi 340i Set, Germany) under constant conditions of 30 ppm lead solution, separation time of 120 min, and at 25 °C.

Experiments were repeated three times. Mean and standard deviation values were calculated. Furthermore, in all experiments, the percentage removal was calculated using the following equation [7]:

$$R(\%) = \frac{(C_0 - C_e) \times 100}{C_0} \quad (1)$$

where C_0 and C_e are the initial concentration of the lead solution and the lead concentration at equilibrium, respectively.

Adsorption capacity of the adsorbent was calculated using (Eq. (2)), and adsorption isotherms were estimated; namely, Langmuir (Eq. (3)) and Freundlich (Eq. (4)) models.

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (2)$$

where C_0 and C_e were defined in Eq. (1), and V and M are the volume (L) of the initial lead solution and mass (g) of the film, respectively. A recorded value of C_e was the average value of three experimental readings.

$$C_e/q_e = 1/bq_m + C_e/q_m \quad (3)$$

$$\log q_e = K_f + 1/n \log C_e \quad (4)$$

where q_m and b are the Langmuir constants, and n and K_f are the Freundlich constants. To study the

adsorption rate, pseudo first and second-orders models of kinetic as expressed by Eq. (5) [15] and Eq. (6) [16], respectively.

$$\log (q_e/q_t) = \log q_e - (k_1 t/2.303) \quad (5)$$

$$(t/q_t) = (1/k_2(q_e)^2) + (t/q_e) \quad (6)$$

where k_1 and k_2 are the adsorption rate constant of pseudo-first and second orders, respectively.

Results and Discussion

The characteristics of the prepared film are summarized in Table 1. Figure 1 shows the SEM images of the FCB in (a), and the film before and after the removal process in (b) and (c), respectively. Regular spherical particles of the furnace carbon black were observed. Before the removal process, some aggregation of the FCB particles was noted of the surface of the film. After removal, shiny particles in star shape were clearly observed on the surface, which can be attributed to the adsorbed lead ions.

TABLE 1. The characteristics of the thin film

Surface area (m ² /g)		Tensile strength (MPa)
Langmuir	BET	
33.18	21.76	21.6

Figure 2 shows the thermogravimetry curve of the film, which provides information about the thermal stability of the film. The thermal degradation of the film occurs in one step, from about 390 to 450 °C, while the polymer from 388.07 to 423.9 °C. It was notable that the nanocomposite film was more thermally stable than the original polymer itself, and this may be because the aggregation of the carbon particles acts as a barrier against the diffusion of polystyrene degradation products into gas phase.

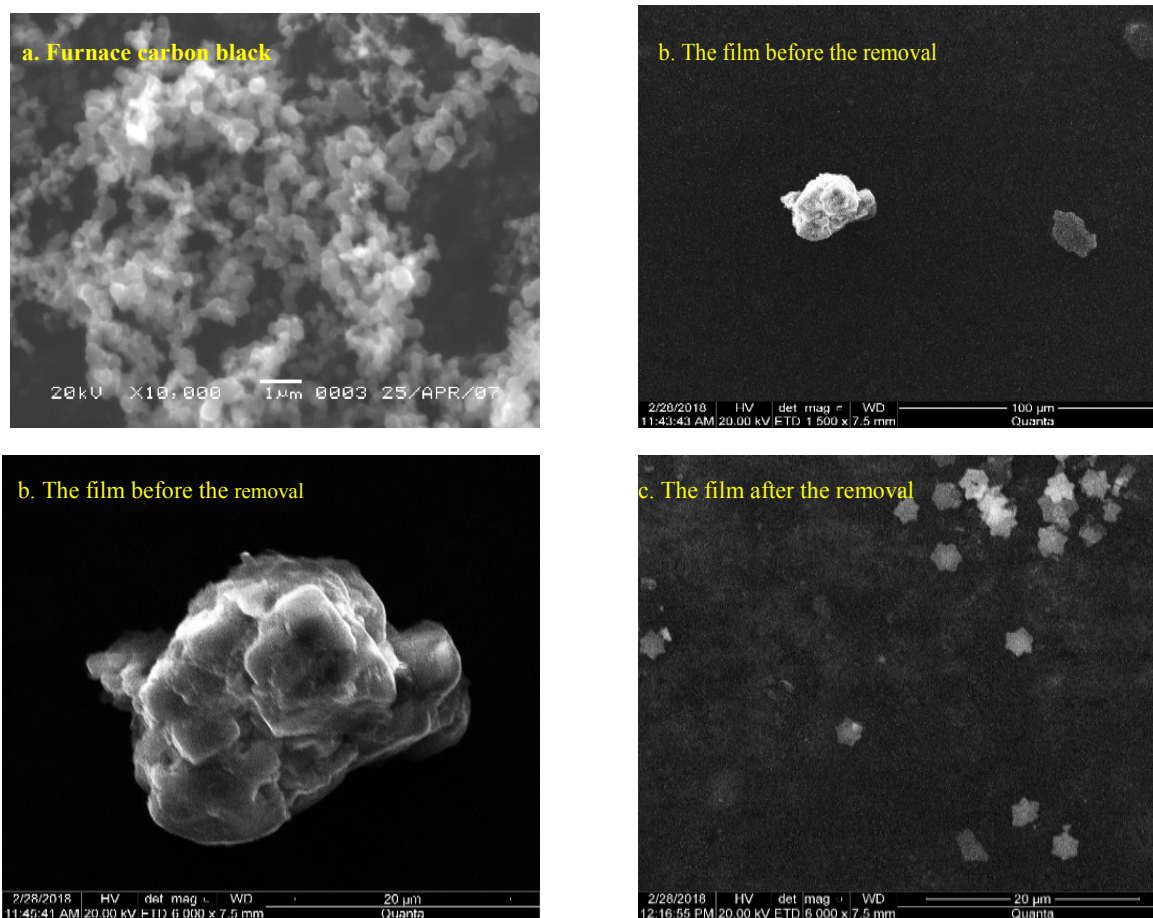


Fig. 1. SEM images of the furnace carbon black in (a), the film before removal (b), and the film after the removal process (c).

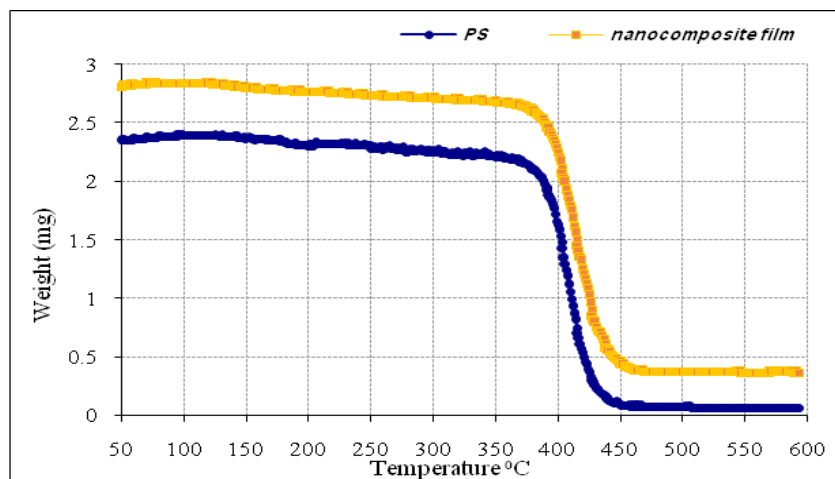


Fig. 2. The thermogravimetry curve of the film.

The lead removal data are summarized in Tables 2-4 and the results are illustrated in Fig. 3-5.

The effect of the initial concentration of lead on its percentage removal is shown in Fig. 3. The lead removal occurs into two steps; the first ends at a lead concentration of 20 ppm followed by the second step. The results suggest more than monolayer adsorption mechanism for the removal of lead ions. In first step, percentage removal increases because of the availability of the adsorption sites on the surface, after which decreases because of saturation the active sites. New surface of adsorption could be formed by this layer; therefore, notable increase in percentage removal with increasing the concentration, forming new layer of adsorption in a second step.

Figure 4 shows the effect of separation time on the lead removal efficiency. Because the active

sites for adsorption have not saturated yet, the percentage removal increases gradually with increasing the separation time until 120 min, then slows due to saturation of the adsorption site [17].

Figure 5 shows the percentage removal of lead as a function of pH. The best medium for lead removal was at pH 6, whereas in the strongly acidic and alkaline media, the percentage removal was reduced. In the acidic medium, protonation process occurred; thereby, the adsorption of protons (H^+) competes with the adsorption of positively charged lead ions [14], whereas in the alkaline medium, the adsorption of lead may be inhibited by the formation of lead hydroxide complex because of the excessive ions of hydroxyl [17], leading to reduce the percentage removal.

TABLE 2. Data of the removal process as a function of initial concentration.

Removal (%)	Standard Deviation	C_e (ppm)	C_0 (ppm)
68.9%	0.06	1.56	5
77.3%	0.49	2.27	10
75.4%	0.26	3.68	15
74.6%	0.85	5.08	20
85.6%	0.78	4.32	30
84.3%	0.57	7.86	50

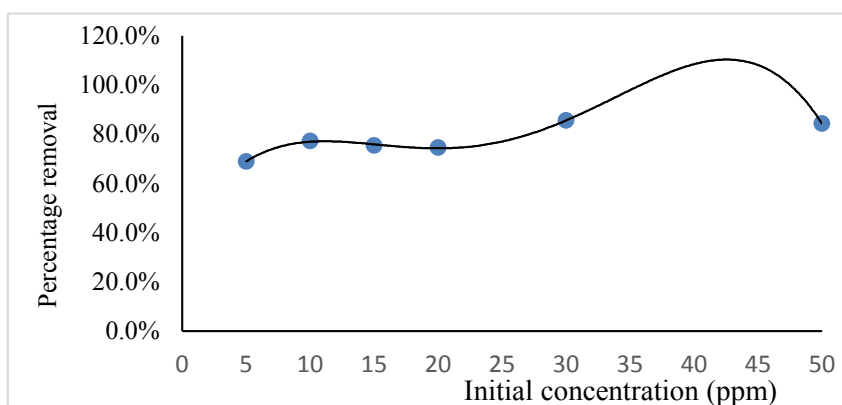
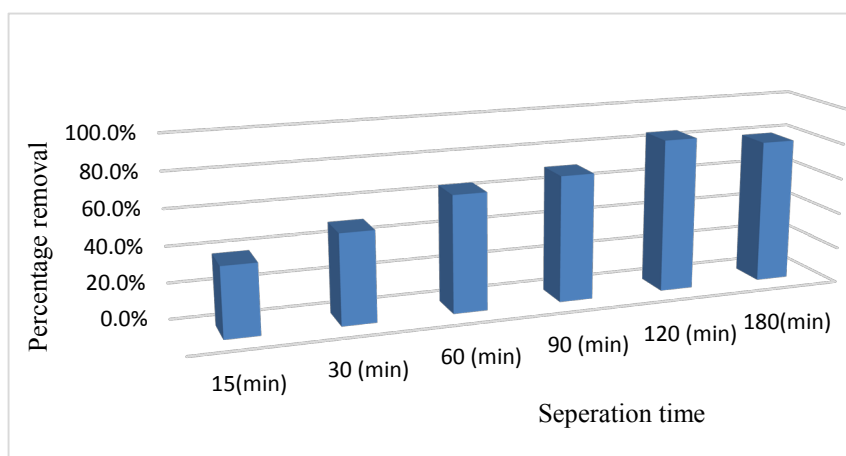
TABLE 3. Data of the removal process as a function of separation time, C_0 was 30 ppm.

Removal (%)	Standard Deviation	C_e (ppm)	Separation time (min)
38.9	0.91	18.32	15
50.1	0.79	14.97	30
65.1	1.00	10.47	60
70.4	1.18	8.87	90
85.6	0.78	4.32	120
80.1	0.87	5.98	180

TABLE 4. Data of the removal process as a function of pH, Co was 30 ppm.

Removal (%)	Standard Deviation	C_e (ppm)	pH
65.1	1.18	10.47	4
71.4	0.79	8.57	5
86.1	0.33	4.18	6
59.7	0.72	12.09	8
49.7	1.87	15.08	9

To determine the underlying mechanism of lead removal, experimental adsorption data were analyzed and described by Langmuir (Eq. (3)) and Freundlich (Eq. (4)) adsorption isotherms models. Plotting (C_e/q_e) vs C_e of the Langmuir model and $\log q_e$ vs $\log C_e$ of the Freundlich model should produce straight lines. The correlation coefficients (R^2) of the linearity relationship govern their suitability for describing the adsorption. A comparison of the obtained R^2 values from both plots 0.5638 for the Langmuir (not shown) and 0.9969 for the Freundlich model (Fig. 6) suggests that the experimental data of lead adsorption best fit the Freundlich model with a K_f of 1.53 mg/g, n of 0.69, and $1/n$ of 1.449.

**Fig. 3. The effect of initial concentration on the removal process.****Fig. 4. The effect of separation time on the removal process.**

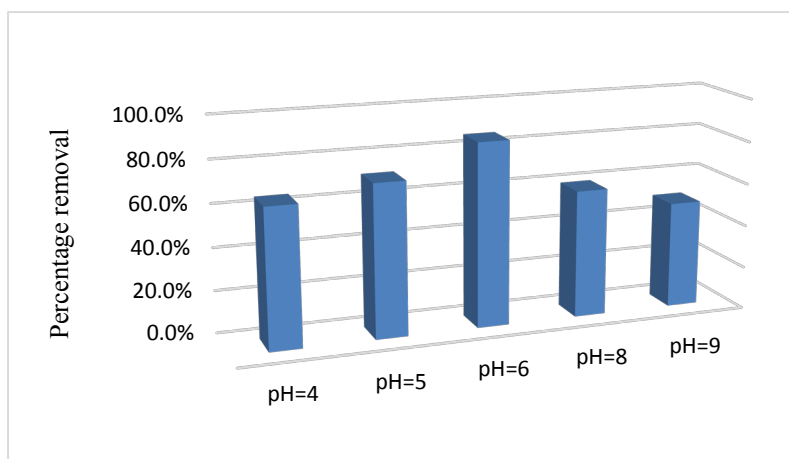


Fig. 5. The effect of pH on the removal process.

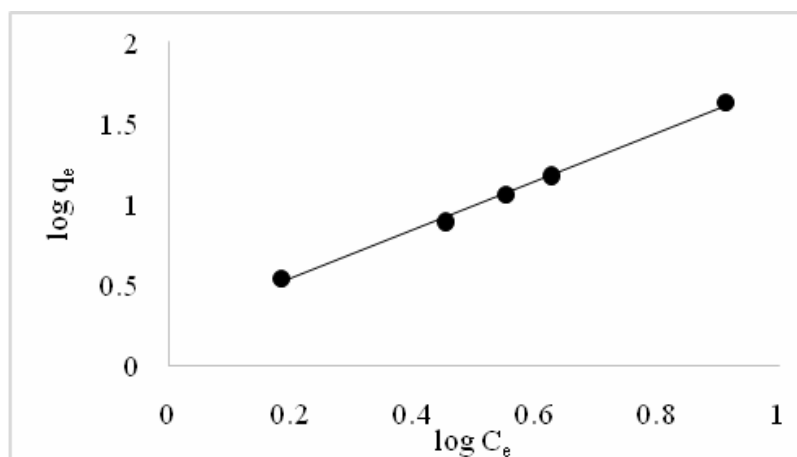


Fig. 6. Plotting of Freundlich isotherm.

Based on the values of $1/n$ and n , cooperative adsorption occurred because the value of $1/n$ was >1 [18]; the adsorption type was chemical adsorption because the value of n was < 1 [20 cited in 19]. These results and those of the lead concentration factor, which suggested more than monolayer adsorption for the removal process, are in agreement and suggest that chemical adsorption occurred on the first layer followed by physical adsorption on the other layers.

The kinetic studies of the adsorption rate were described by pseudo first-order kinetics, as expressed by Eq. (5) and pseudo second-order kinetics, as expressed by Eq. (6). Their applicability for describing the kinetics of the lead adsorption was determined by examination of the *Egypt.J.Chem.* 62, No. 1 (2019)

correlation coefficients (R^2).

Plotting the pseudo first-order model yielded a straight line with a correlation coefficient (R^2) of 0.7573 (not shown), indicating that the adsorption rate did not follow this model.

On the other hand, plotting the pseudo second-order model yielded a linear relationship with a R^2 value of 0.985, indicating that the adsorption rate was described accurately by this model (Fig. 6). The value of K_2 was 0.044559 g/mg min and the calculated value of q_e was 20.00 mg/g. Notable agreement was observed between the calculated and experimental (19.61 mg/g) values of q_e , confirming the suitability of the model for describing the adsorption rate.

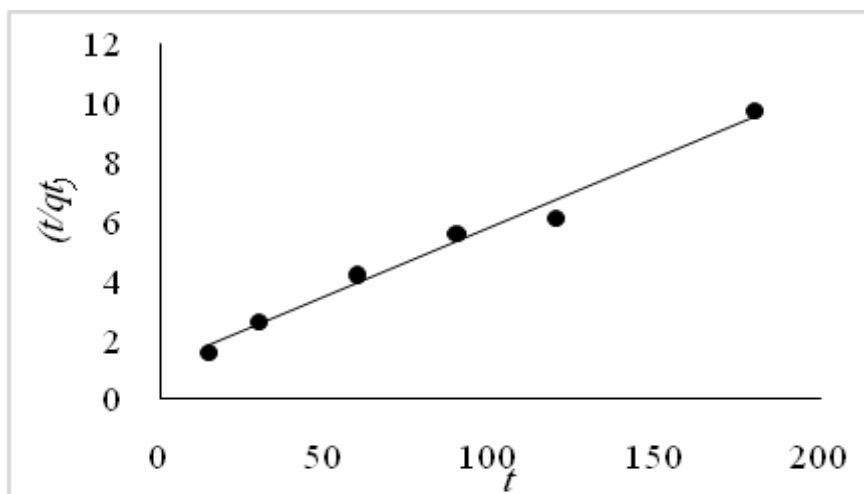


Fig. 7. Plotting of pseudo second-order model.

Conclusion

Preparation and characterization of nanocomposite films from polystyrene as a matrix and FCB as a filler was performed to investigate their ability to remove lead from an aqueous solution. The major conclusions can be summarized in the following points:

- The best conditions for removal were 30 ppm lead with a 120 min separation time at pH 6.
- To describe the adsorption data, the Freundlich isotherm was the best model.
- The adsorption rate followed pseudo second-order kinetics.

Thus, it can be concluded that the prepared nanocomposite films are effective materials for the removal of heavy-metal water pollutants, specifically, the lead ion.

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إزالة المعادن الثقيلة باستخدام أغشية رقيقة لمتراكبات متعدد ستيرين البوليمرية النانوية

مشاعل الشبانات

جامعة الأميرة نورة بنت عبدالرحمن - كلية العلوم - قسم الكيمياء - الرياض - السعودية.

تم تحضير أغشية رقيقة لمتراكبات بوليمر تتكون من متعدد ستيرين وأسود الكربون (الفرن) لاستخدامها كمواد مازة لإزالة المعادن الثقيلة من مياه الصرف الصناعي. وقد تم توصيف خواص الغشاء، ودراسة تأثير عدد من العوامل على عملية الإزالة وهي: التركيز الابتدائي، زمن الفصل، pH الوسط. وقد وجد أن أفضل الظروف لعملية الإزالة باستخدام الغشاء هي عند زمن فصل يبلغ 120 دقيقة، و pH=6، وتركيز ابتدائي = 30 ppm. وأظهرت نتائج دراسة الامتزاز أن نموذج امتزاز فرندلش هو المناسب لوصف الامتزاز، ومعدل الامتزاز حركياً يتبع الرتبة الثانية الكاذبة.