Polyurethane foam-cadmium sulfide nanocomposite with open cell structure: Dye removal and antibacterial applications

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Abstract−A new way to synthesize open cell polyurethane foam using cadmium ions has been described. By converting to cadmium sulfide nanoparticles, cadmium ions have been fixed on the open cell polyurethane foam. Open cell polyurethane foam containing CdS nanoparticles (PUF-CdS) was characterized by X-Ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). The SEM results showed foam containing nanoparticles unlike pure foam (PUF) has an open cell structure. In the following, the applicability of synthesized nanocomposite in wastewater treatment was investigated. The dye removal efficiency of PUF-CdS was investigated with the objective of removing Reactive Orange 122 (RO122) as a model pollutant from aqueous solution. The effects of adsorbent dosage, initial dye concentration and initial pH of solution on RO122 removal were studied. Kinetics and equilibrium isotherms for adsorption of dye on PUF-CdS were analyzed. The maximum adsorption capacity obtained from Langmuir isotherm equation was 22.7 mg g^{-1}. The experimental data were adjusted to the pseudo-second-order kinetic model. The antibacterial activity of PUF-CdS was also investigated against *E. coli* and *S. aureus*.

Keywords: Polyurethane Foam, Adsorption, Dye, Antibacterial Properties, Cadmium Sulfide

INTRODUCTION

The removal of pollutions from aqueous medium is important both industrially and environmentally. The application of the adsorption process has assumed remarkable importance in water treatment [1,2]. For reasons of polar and non-polar groups, high specific surface area, light weight, porous structure, highly stability, extremely low cost and excellent mechanical strength, the polyurethane foams (PUFs) are excellent sorbent materials for removal of various pollutions from aqueous medium [3,4]. The first application of PUF as a solid sorbent for preconcentration and separation started in 1970, and the first application of PUF for online preconcentration and determination was reported in 1998 [5]. After these works, a fast increase in the number of published papers was observed [6-8].

From the reaction between of polyols and diisocyanates in the presence of one or more blowing agents, PUF$_S$ are prepared. These polymers are classified into two groups of open and closed cell. In the open cell foams, in contrast to the closed cell, the cell walls or surfaces of the bubbles are broken [9]. The open cell structures compared to the closed cell structures provide a larger specific area for adsorption. So the open cell structures compared with closed-cell will be more efficient to adsorb pollutants [10].

Cell opening in polyurethane foams is a complex process. Several hypotheses have been proposed for the cell opening mechanisms in the literature. In the following are some of the cell opening mechanisms listed: Urea precipitation defoaming (solid particle de-

foaming), surfactant phase separation, foam matrix viscosity rise, spontaneous film rupture mechanism and chemical cell opener with hydroxyl group [11,12]. Harikrishnan et al. have reported the role of nanoclays as cell opener in the synthesis of PUF-clay nanocomposite [13].

The present research introduces a new way for the synthesis of open cell flexible polyurethane foam by modifying of closed cell polyurethane foam formulation using Cd^{2+} ions. In the following, for stability of Cd^{2+} ions in the foam structure, they were converted to CdS nanoparticles.

The utilization of CdS nanoparticles has received much attention, as they have a variety of applications in fields such as photochemical catalysis, gas sensor, detectors for laser and infrared, solar cells, nonlinear optical materials and various luminescence devices [14]. Also, in the last decade, the ability of metal sulfides and oxides such as CdS, TiO$_2$, ZnO, CuO, Fe$_3$O$_4$ and so on, has been reported in water treatment and disinfection [15-17]. But, the exact mechanisms for the action of these nanoparticles on microorganisms are not fully understood, and in this case there are only hypotheses [18]. Electrostatic interactions, production of free radicals, modulation

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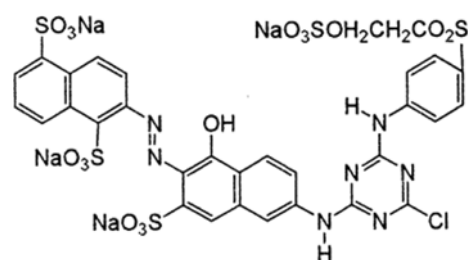
Scheme 1. Chemical structure of the textile dye RO122.

of phosphotyrosine of proteins, interaction with SH groups and phosphorus containing molecules (DNA) are the most important hypotheses [19,20].

The main objective of the present research was to study the efficiency of prepared PUF containing CdS nanoparticles (PUF-CdS) with open cell structure in removal of Reactive Orange 122 ($C_{31}H_{20}ClN_7Na_4O_{16}S_5$), (Scheme 1) as a model dye. The antibacterial capability of prepared foam was also investigated against Gram-positive and Gram-negative bacteria to indicate its performance for inactivating of microorganisms in drinking water as chlorine but without forming carcinogenic byproducts.

MATERIALS AND METHODS

1. Materials

$Cd(NO_3)_2 \cdot 4H_2O$ and Thiourea were purchased from Merck Co. NaOH was obtained from Sigma Aldrich Co. YUKOL 4813 Polyol (46-50 mg KOH g^{-1} and 3,500 g mol^{-1}) and KONIX KE-878N copolymer polyol (28-32 mg KOH g^{-1}) were obtained from SKC Co. and KPX Chemical Co. Ltd, respectively. Toluene diisocyanate (TDI) was obtained from Karoon Petrochemical Co., Iran. Dabco 33-LV, KOSMOS 29 and Niax Silicone surfactant L-620 as surfactant, catalysts used for the synthesis of foam were purchased from Air Products and Chemicals, Degussa and General Electric Company, respectively.

2. Preparation of PUF and PUF-CdS

The flexible polyurethane foams were synthesized in a laboratory

scale by one-shot method [3]. The composition, formulations and physical properties of prepared foams are given in Table 1. For the preparation of PUF, KONIX FA-717, KONIX KE-878N, distilled water, DABCO 33-LV catalyst, Kosmos 29 and Silicone surfactant were stirred at 600 rpm for 2 min as the A component. TDI as B component added to the A component and mixed at 3,000 rpm for 8 s to reach cream time. Immediately after mixing, the mixture was poured into an open mold (15 cm×15 cm×15 cm) and allowed to rise freely. The cream time, gel time and rise time for preparation of PUF were 9, 60, 65 s, respectively. The prepared PUF was cured for 72 h at the room temperature.

For the preparation of PUFs containing of CdS nanoparticles, called here PUF-CdS foams, in the A component instead of the distilled water, 1.25 M Cd $(NO_3)_2$ solution were used. Then the same route described above was followed. The prepared PU-Cd $(NO_3)_2$ foams soaked in a solution of 0.5 M of thiourea and then added 2 M NaOH solution (the volume ratio 1 : 1) and were heated at 75 °C for 90 min. At this point the color change of foam contains cadmium ions from white to yellow, conforms synthesis of CdS nanoparticles. This synthesis is shown in Scheme 2, briefly.

3. Dye Removal Experiments

All batch adsorption tests were in a 100 mL beaker on a stirrer. The stirring speed was maintained at 500 rpm. Various parameters such as the effects of PUF-CdS adsorbent dosages (0.05, 0.10, 0.15, 0.20 and 0.25 g), initial dye concentrations (10, 20, 30, 40 and 50 mg L^{-1}) and initial pH (1 to 9) were investigated [3]. The concentration of dye in solution was determined by spectrophotometry at 488 nm in time intervals previously established using analytical curve approach.

The removal percentage (R) of dye was calculated using Eq. (1):

$$R\,(\%) = ((C_o - C_t)/C_o) \times 100 \qquad (1)$$

in which C_o is the initial concentration of dye and C_t is the concentration of dye in the solution at a given time.

RO 122 was removed four times to assess the potential reusability of PUF-CdS adsorbent. Before each cycle, a desorption experiment was performed by putting the removed PUF-CdS adsorbent into a clean flask containing 100 mL water, and the pH was adjusted to 11. The flask was kept under stirring for 2 h. The PUF-CdS adsorbent was then washed three times with deionized water before the initiation of the next adsorption cycle.

4. Antibacterial Tests

Antibacterial activity of the prepared PUF-CdS was conducted against *E. coli* ATCC 25922 and *S. aureus* ATCC 25923 using "plate

Table 1. Formulation and some physical properties of PUF-CdS

Component	PUF	PUF-CdS
Polyether polyol (KONIX FA-717)	57.6 g	57.6 g
Polymeric polyol (KONIX KE-878N)	14.4 g	14.4 g
Distill water	2.16 g	-
Dabco 33-LV	0.280 g	0.280 g
Kosmos 29	0.300 g	0.300 g
Niax Silicone L-620	0.675 g	0.675 g
2,4- and 2,6-toluene diisocyanate (TDI)	30.0 g	30.0 g
(1.25 M)Cd$(NO_3)_2$	-	2.16 g
Density	50 (kg/m^3)	52 (kg/m^3)
Cream time	9 s	12 s
Gel time	60 s	58 s
Rise time	65 s	73 s
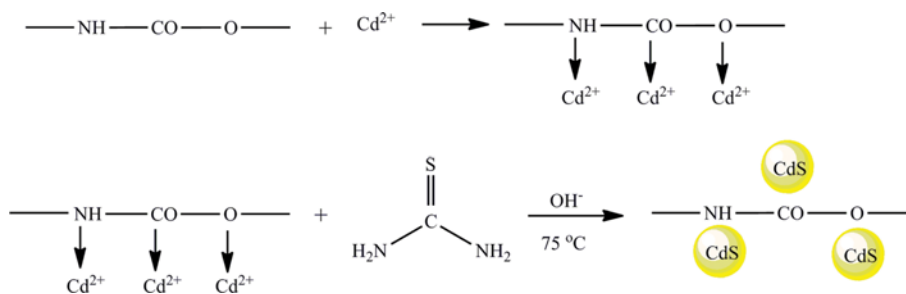
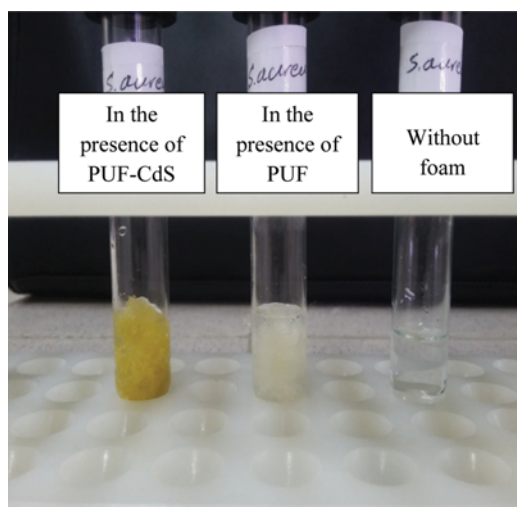**Scheme 2. Schematic illustration of synthesis of open cell PUF-CdS.**

Fig. 1. Antibacterial test method.

counting method" [21]. Nutrient agar was used as the growing medium. All glassware was sterilized at 120 °C for 15 min. Bacteria was grown aerobically at 37 °C for 24 h. For the antibacterial test, PUF and PUF-CdS were immersed in bacterial water (10^5 colony-forming units (CFU)/mL); then after 0, 3, 6, 9 and 12 h, the number of survivor bacteria was determined in 20 μL of the sample (Fig. 1) [21,22].

5. Characterization of Open Cell Flexible PUF-CdS Nanocomposite

The crystalline structures of CdS nanoparticles on PUF surface were characterized using X-ray diffraction (XRD; Siemens D-5000 diffractometer, Germany) with CuK$_\alpha$ radiation (λ=0.15418 nm) at 30 kV and 15 mA. The cell and surface morphology of PUF and PUF-CdS nanocomposite were evaluated using SEM with gold coating.

RESULTS AND DISCUSSION

1. Characterization

The X-ray diffraction (XRD) pattern was used to confirm the successful deposition of CdS crystals on the polyurethane foam. In
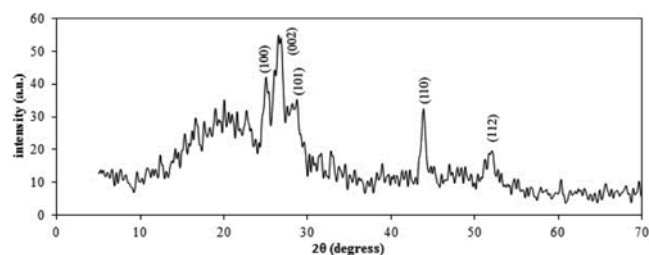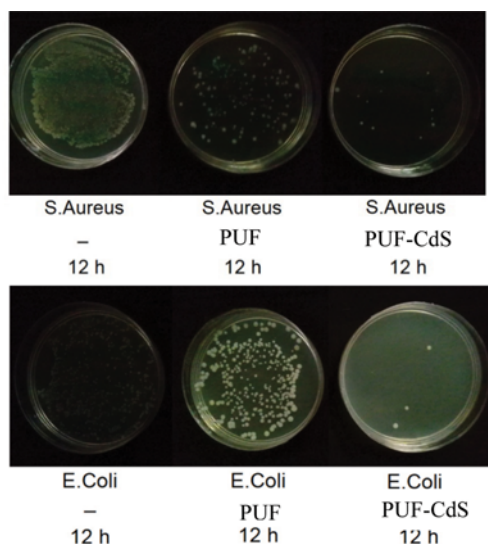

Fig. 2. XRD pattern of PUF-CdS nanocomposite.

Fig. 2, the diffraction peaks at 2θ of 25°, 26.4°, 28°, 43.7° and 51.2° are distinctly indexed to the crystal planes of hexagonal wurtzite CdS (JCPDS No. 41-1049) [23].

The morphology of PUF and PUF-CdS was examined by scanning electron microscopy (SEM) (Fig. 3). Fig. 3(a) shows that the PUF-CdS has open and partially opened cell structure and the number of closed cell in PUF-CdS is nearly zero. Fig. 3(b) indicates cell walls in PUF-CdS. At a glance, it is obviously seen that the CdS nanoparticles are located in cell walls. The formation of open cell structure in PUF-CdS nanocomposite could be attributed to the
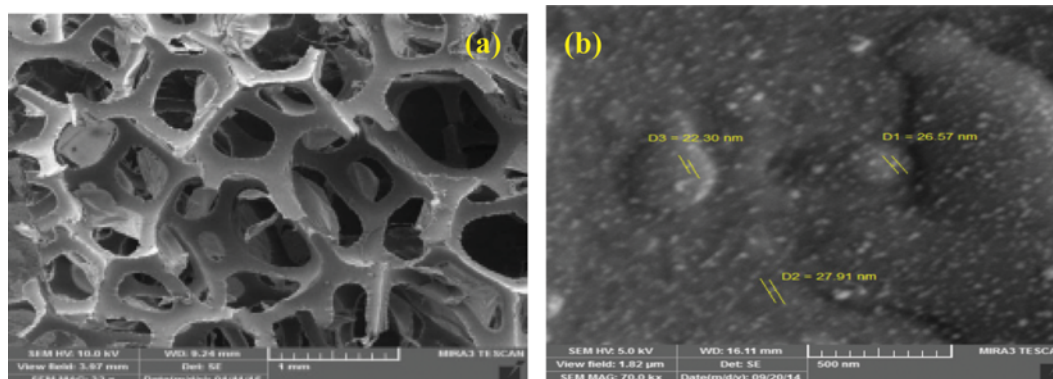

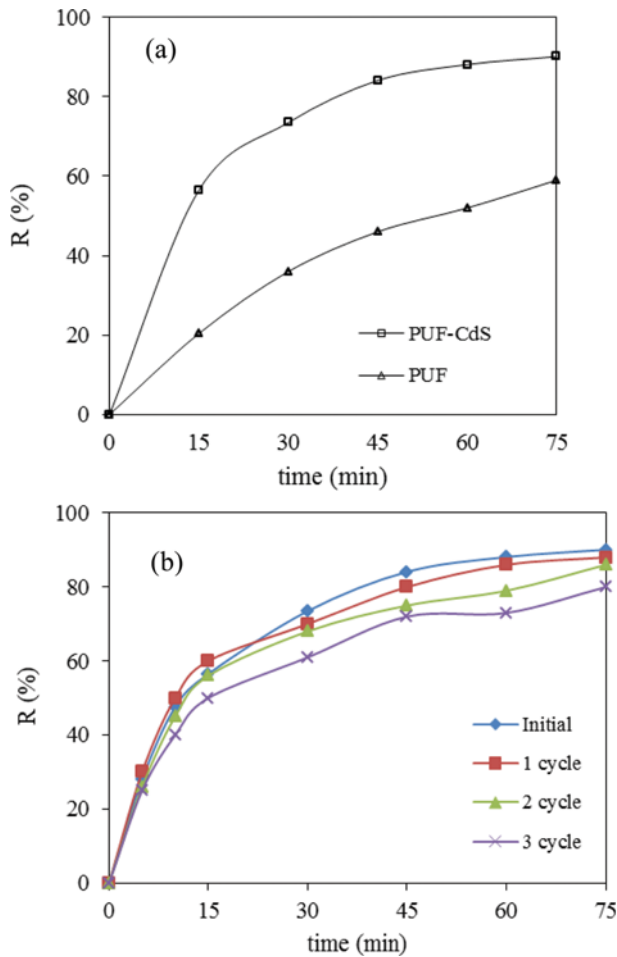**Fig. 3. SEM images of (a) PUF-CdS and (b) PUF-CdS shell wall.**

Fig. 4. (a) Dye removed efficiency of PUF and PUF-CdS (b) Reusability test results of the 3 cycles of RO122 dye decolorization experiments ([dye]$_o$=30 mg L^{-1}, pH=1, W$_{adsorbent}$=0.15 g).

Fig. 5. The effect of initial pH on dye removal efficiency of PUF-CdS nanocomposite (time=75 min, [dye]$_o$=30 mg L^{-1}, W$_{adsorbent}$=0.15 g).

may be utilized repeatedly for dye decolorization of wastewater in textile and paint industry.

2-1. The Effects of Operational Parameters

The pH of a solution is one of the most important parameters affecting the adsorption process. The influence of pH on dye removal efficiency of prepared foams was investigated over the pH range from 1 to 9 (Fig. 5). It is obvious from Fig. 5 that the removal of RO122 increases with decreasing of pH. Interaction between RO122 and PUF-CdS could play an important role on dye adsorption at various pH values. Proposed mechanism for the effect of pH can be in accordance with solvation phenomena that non-bonding orbital electron pairs of the nitrogen, oxygen and sulfur atoms have the capability to take hydronium ion at low pH values on PUF-CdS. Therefore, the positive charge created by hydronium ion on PUF-CdS can to neutralize the negative charge of RO122 through electrostatic force generated between two opposite charges (PUF-CdS$^+$ and RO122$^-$). As pH of the system decreased, the number of positive charged adsorbent sites increased, and the number of negatively charged surface sites decreased, which did favor the adsorption of negatively charged RO122 ions. With increasing in pH

generation of bonds between Cd^{2+}---water, and Cd^{2+}---TDI that delays the blowing reaction. The late stage generation of carbon dioxide (i.e., blowing reaction between water and TDI) occurs when the temperature rises due to the exothermic polymerization reaction becoming sufficient to break the generated bonds. This late stage has been argued to be the mechanism of cell opening [13,24,25,26].

2. Dye Removal Efficiency of PUF-CdS

Typical adsorption of PUF and PUF-CdS adsorbents was recorded upon exposure to 30 mg L^{-1} RO122 concentration at pH 1 (Fig. 4(a)). The results indicated that PUF-CdS nanocomposite is an excellent adsorbent in comparison to PUF. This can be related to the high surface area of PUF-CdS in comparison with PUF since opening PUF-CdS cells. It can be seen from Fig. 4(a), the adsorption step took 75 min and the removal percentage of dye reached the value of 90.

For practical applications, the level of reusability is an important issue. Dye decolorization capabilities of reused PUF-CdS nanocomposites were tested for three cycles of reuse (Fig. 4(b)). After the three cycles of regeneration, favorable % removal of RO122 was 80, which suggests that PU foam containing CdS nanoparticles can sustain their decolorization capacity under several cycles of reuse and
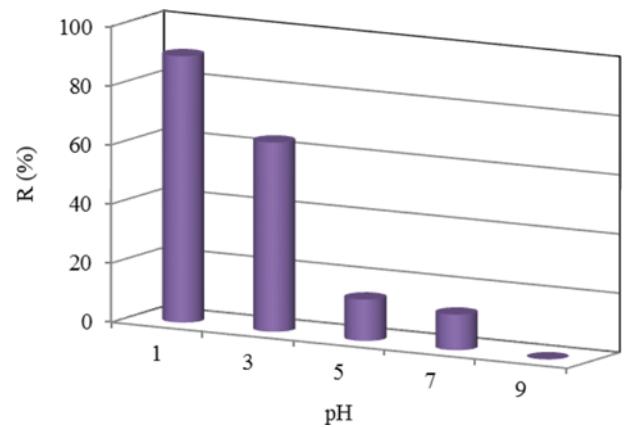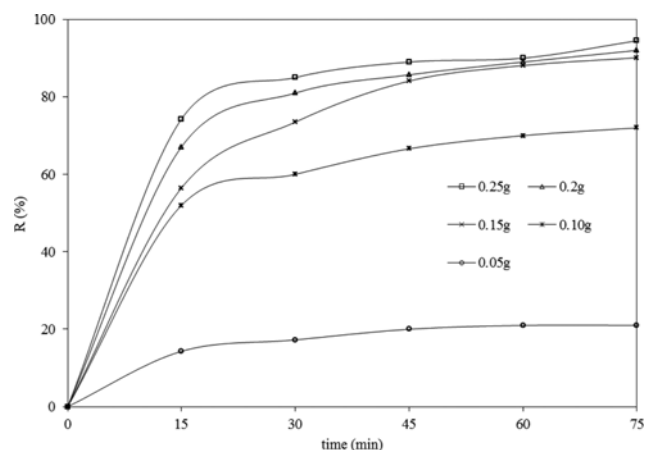

Fig. 6. The effect of adsorbent dosage on dye removal efficiency of PUF-CdS (pH$_{initial}$=1, [dye]$_o$=30 mg L^{-1}).
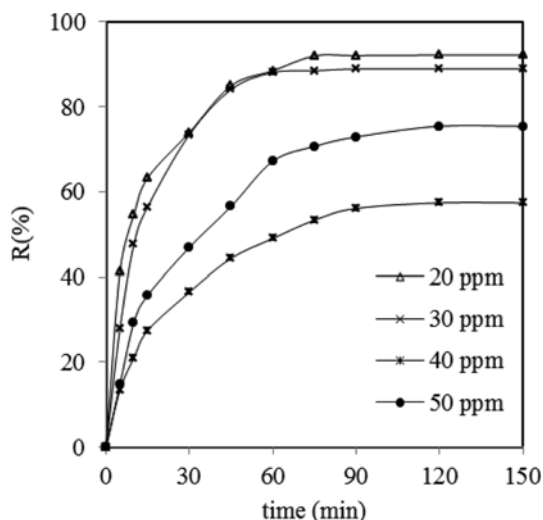
Fig. 7. The effect of initial dye concentration on dye removal efficiency of PUF-CdS (pH=1, $W_{adsorbent}$=0.15 g).

value, hydroxyl groups (OH^-) increase, resulting in repulsion between anionic dye and PUF-CdS surface; hence, a significant decrease in dye adsorption occurs at higher pH.

The effect of adsorbent dosage on dye removal efficiency of PUF-CdS is illustrated in Fig. 6. As can be seen, the dye removal efficiency of PUF-CdS increases with increasing the amount of PUF-CdS adsorbent. This can be related to the increasing of adsorbent surface area and the availability of more positions of the absorption sites, which causes an increase in dye removal efficiency of PUF-CdS.

From Fig. 7, the removal percentage of RO122 by a constant amount of PUF-CdS decreases with the increase in initial dye concentration. PUF-CdS has a fixed number of adsorbing sites that become saturated over a definite concentration. At low dye concentrations, the ratio of adsorbing sites present on PU-CdS to the total RO122 molecules in the solution is higher, and hence, all the RO122 molecules may attach with the active functional groups and removed from the solution. On the other hand, by increasing RO122 concentrations, the number of active adsorption sites is not sufficient to lodge all the dye molecules so, it causes a decreasing of the RO122 removal percentage.

2-2. Kinetic and Isotherm Characterization

Kinetic studies of the adsorption process can provide important information about their behavior, such as the time required to attain equilibrium, the adsorption rate, and the prediction of sol-

ute concentration in each phase after equilibrium is reached. Also, such data are important in the understanding of the influence of some practical variables on the adsorption process [27,28].

The kinetic parameters of RO122 adsorption onto PUF-CdS are given in Table 2. The correlation coefficient obtained from the pseudo-second-order model is higher than the other investigated model for the adsorption of dye. Therefore, the pseudo-second-order model could better describe the kinetics of the adsorption of RO122 on PUF-CdS without determining the rate-limiting step. The boundary layer (film) or the intra-particle diffusion of solute on the solid surface from bulk of solution may be the rate-limiting step [29,30].

An intra-particle mass transfer diffusion model proposed by Morris-Weber model (Table 2) is useful for determining whether a diffusion process is the limiting step of the adsorption rate [27]. In the Morris-Weber model, C gives an idea about the boundary layer thickness, that is, the larger the value, the greater the boundary layer effect [31]. Based on the results reported in Table 2, it may be concluded that adsorption of RO122 onto PUF-CdS follows the Morris-Weber model. However, the linear plot does not pass through the origin, indicating that the intra-particle is not the only rate-determining step [30]. This indicates that the mechanism of dye adsorption onto PUF-CdS is complex and both the film and intra-particle diffusion contribute to the rate-determining step.

Adsorption process can be also modeled by application of equilibrium adsorption isotherms, which provide a useful mathematical description of the adsorption capacity after equilibrium is reached. Also, the equations of such isotherms allow the comparison of different adsorption systems operated at different experimental conditions [2].

Linear regression of the RO122 sorption data was done by use of Langmuir (Eq. (2)), Freundlich (Eq. (3)) and Dubinin-Radushkevich (Eq. (4) and (5)) isotherm models.

$$\frac{1}{q_e} = \left(\frac{1}{q_m K_L}\right)\left(\frac{1}{C_e}\right) + \frac{1}{q_m} \tag{2}$$

$$\ln q_e = \ln K_F + \left(\frac{1}{n_F}\right)\ln C_e \tag{3}$$

$$\ln(q_e) = \ln(q_s) - k_{ad}\varepsilon^2 \tag{4}$$

$$\varepsilon = RT\ln\left[1 + \frac{1}{C_e}\right] \tag{5}$$

where, q_e (mg g^{-1}) is the amount of solute retained on the adsorbent at equilibrium, C_e (mg L^{-1}) is the concentration of solute that

Table 2. Evaluation of the kinetic models for the adsorption of RO122 on PUF-CdS

Kinetic model					
Lagergren-first-order		Pseudo-second-order		Intra-particle diffusion	
$\log(q_e - q_t) = \log q_e - \left(\dfrac{k_1}{2.303}\right)t$		$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^2} + \dfrac{t}{q_e}$		$q_t = kt^{0.5} + C$	
k_1 (min^{-1})	0.069	k_2 (g mg^{-1} min^{-1})	0.0036	k (mg g^{-1} min$^{-0.5}$)	2.34
q_e (mg g^{-1})	21.7	q_e (mg g^{-1})	21.32	C (mg g^{-1})	0.942
R^2	0.975	R^2	0.999	R^2	0.973

remained in the solution at equilibrium, q_m (mg g^{-1}) is the maximum adsorption capacity of monolayer, K_L (L mg^{-1}) is the Langmuir model constant, K_F (mg g^{-1}) (L mg^{-1})$^{1/n}$ is the constant indicative of the relative sorption capacity of the sorbent, 1/n is the Freundlich constant, q_s (mg g^{-1}) is a constant in the Dubinin-Radushkevich isotherm model which are related to adsorption capacity; K_{ad} (mol^2 kJ^{-2}) is a constant related to the mean free energy of adsorption; R (J mol^{-1} K^{-1}) is the gas constant; and T (K) is the absolute temperature [27,30,32,33].

The values of the constants obtained for the three models are presented in Table 3. When the correlation coefficients of the two isotherm models are compared, it can be seen that both of them are greater than 0.95. So, it is very difficult to prefer a certain isotherm model to fit the adsorption data. To identify a suitable isotherm model for the adsorption of dye on PUF-CdS, chi-square analysis has been carried out. The equivalent mathematical statement is

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \qquad (6)$$

where $q_{e,m}$ is equilibrium capacity obtained by calculating from the model (mg g^{-1}) and q_e are experimental data of the equilibrium capacity (mg g^{-1}) [30,33]. The results of χ^2 are given in Table 3. The fit is good when χ^2 is a small number. The lower χ^2 value of Dubinin-Radushkevich isotherm can be considered as best fitting model for the adsorption of RO 122 on PUF-CdS.

The "Langmuir parameter" (R_L) obtained from Langmuir isotherm model is used for prediction of the favorability of adsorption process. An isotherm is considered to be unfavorable ($R_L > 1.0$), linear ($R_L = 1.0$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0.5$) depending on the value of R_L [30,34]. For the present adsorption system, R_L value is 0.024-0.058, indicating that the adsorption equilibrium

Table 3. Isotherm constants for RO122 adsorption on PUF-CdS

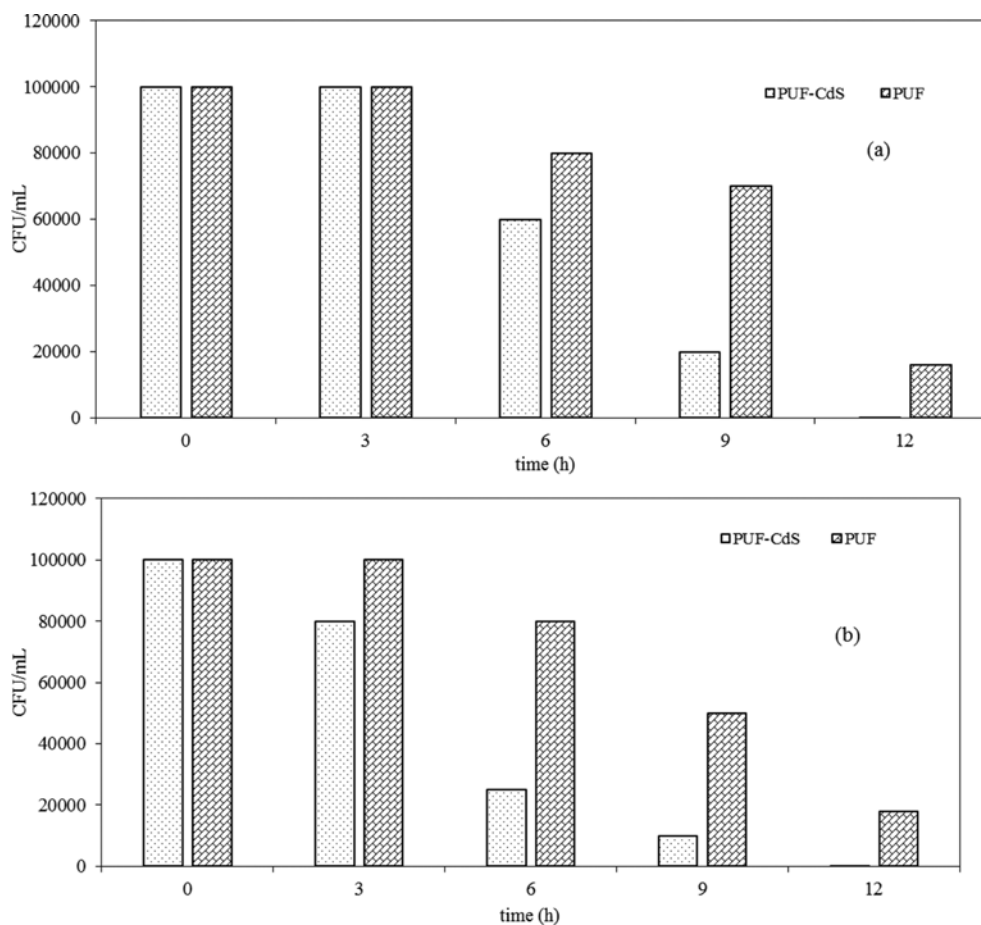| Isotherm model	Langmuir	Freundlich	Dubinin-Raduskevich
Constants	q_m=22.7 (mg g^{-1}) K_L=0.798 (l mg^{-1}) R^2=0.95 χ^2=0.0011	K_F=12.45 (mg g^{-1}) (l mg^{-1})$^{1/n}$ n=5.48 R^2=0.76	q_e=22.2 (mg g^{-1}) k_{ad}=634×10^{-8} R^2=0.98 χ^2=0.0045

Fig. 8. Antibacterial ability of PUF and PUF-CdS against of (a) *E. coli* (b) *S. aureus*.

was favorable.

2-3. Adsorption Thermodynamics

A thermodynamic characterization of RO122 adsorption on PUF-CdS was carried out by evaluating the extraction efficiency at different temperatures (25, 30, 40, 50 and 60 °C).

The equilibrium constant (K_c) was calculated for each temperature investigated using the following equation [2]:

$$K_c = \frac{c_{ads}}{C_e} \tag{7}$$

where C_{ads} (mg L^{-1}) is the amount of dye adsorbed onto PUF-CdS at equilibrium and C_e (mg L^{-1}) is the dye concentration at solution in the same condition.

According to the van't Hoff equation (Eq. (8)) a linear fit must be obtained when $1/T$ (T in K) is plotted versus log K_c over the entire range of temperature investigated.

$$\log K_c = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \tag{8}$$

where T is the absolute temperature (K) and R is the ideal gas constant (J K^{-1} mol^{-1}) [2]. A linear fit with an equation of log K_c=−981 (1/T)+4.33 (R^2=0.96) was obtained. ΔH and ΔS were found to be 18.8 kJ mol^{-1} and 82.9 J mol^{-1} k^{-1}, respectively. The value of ΔG was derived from K_c using ΔG=−RTlnk, and it was −25.0 kJ mol^{-1} at 298 k. The negative value of ΔG and positive value of ΔH indicated that the adsorption process was spontaneous and endothermic.

3. Antibacterial Activity of Prepared Foams

The time course of *E. coli* and *S. aureus* inactivation by PUF and PUF-CdS is illustrated in Fig. 8. The results indicate that 0.05 g mL^{-1} of PUF-CdS inhibits the growth of *E. coli* after 9 h, but in the case of *S. aureus*, there is a significant inhibitory in growth after 6 h. From Fig. 8, the antibacterial activity of PUF and PUF-CdS is clear; however, this effect is greater in PUF-CdS that represents the antibacterial role of CdS nanoparticles. There is no exact mechanism for the bactericidal effect of CdS nanoparticles but damage to cellular enzymes, DNA and bacterial cell walls by nanoparticles, and too release of cationic ions and their interaction with the cell walls and intracellular contents can be proposed for bactericidal effect of metallic nanoparticles like CdS nanoparticles. PUF antibacterial effect can be attributed to the presence of catalysts such as 1,4-Diazabicyclo [2.2.2] octane and Di-butyl tin dilaurate within the PUF structure, which were used during the preparation of foam. The bacteria could be probably killed because of pH increase or release of cationic ions (Sn^{2+}) due to presence of 1,4-Diazabicyclo [2.2.2] octane and Di-butyl tin dilaurate in the foam structure.

CONCLUSIONS

The present research reports a new way to synthesize open-cell flexible polyurethane foam using Cd^{2+} ions. SEM images show Cd^{2+} can be used as a chemical PUF$_S$ cell opener. The prepared PUF-CdS foam was used as an adsorbent for removal of RO122 as a model pollutant from aqueous solution. The effects of various parameters were studied. The equilibrium adsorption data were modeled using the Langmuir and Freundlich isotherms. The adsorption

isotherms were well fitted by the Langmuir isotherm (R^2=0.95). The maximum adsorption capacity obtained from Langmuir isotherm equation was 22.7 mg g^{-1}. The experimental data were adjusted to the pseudo-second-order kinetic model. The application of Morris-Weber model indicated that both film diffusion and intraparticle diffusion processes were active during the adsorption of RO122 on PUF-CdS. Also, the prepared foam displays antibacterial capability toward the gram-negative bacterium, *E. coli*, and grampositive *S. aureus*.

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