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Araştırma / Research

Preparation of Dextran Cryogels and Some of Their Applications

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Abstract

In this study, dextran (DEX) cryogels were prepared using 50% divinyl sulfone (DVS) crosslinker based on the repeating unit of DEX, under cryogenic conditions via cryogellation technique. It was shown that DEX cryogels can be used as column fillers to remove toxic substances such as organic dye, methylene blue (MB), pesticide, and paraquat (PQ) which are harmful to the environment and human health. The maximum absorption capacity of 15 mg DEX cryogels was determined as 10.69±0.14 mg/g using 5 mL of 100 ppm MB dye in about seven minutes, and as 2.87±0.33 mg/g from 5 mL of 40 ppm PQ pesticide in about ten minutes. The reusability of DEX cryogel for MB was also examined. In the consecutive use of DEX cryogel weighing ~30 mg, initially cryogel absorbed 6.43±0.15 mg MB/g cryogel from 20 ppm 30 mL MB dye, but this value decreased to 4.71±0.48 mg MB/g cryogel after the fifth use. The same cryogel released the same amount of MB dye after the first use of 3.78±0.33 mg MB/g cryogel, but after the fifth use the release amount decreased to 0.92±0.38 mg MB/g cryogel upon treatment with 1 M 30 mL HCl solution. The adsorption kinetics of DEX cryogel for MB were also examined and the Langmuir isotherm model with a correlation coefficient of 0.9983 and the K_L value of 0.36, representing the best fit amongst the other well-known models such as the Freundlich isotherm, Temkin, Elovich and Dubinin-Radushkevich.

Keywords: dextran cryogel, dye and pesticide removal, natural polymer, superporous/macro porous material.

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Dekstran Kriyojellerinin Hazırlanması ve Bunların Bazı Uygulamaları

Öz

Bu çalışmada, dekstran (DEX) kriyojeleri, tekrarlayan DEX birimine göre %50 divinil sülfon (DVS) çapraz bağlayıcı kullanılarak kriyojenik koşullar altında kriyojelasyon tekniği ile hazırlanmıştır. DEX kriyojellerinin çevreye ve insan sağlığına zararlı organik boya, metilen mavisi (MB), pestisit, parakuat (PQ) gibi toksik maddeleri uzaklaştırmak için kolon dolgu maddesi olarak kullanılabileceği gösterilmiştir. DEX kriyojelinin 15 mg'ı için maksimum absorpsiyon kapasitesine, MB için yaklaşık yedi dakikada 5 mL-100 ppm çözeltiden 10,69±0,14 mg/g, PQ için ise yaklaşık on dakikada 2,87±0,33 mg/g absorblayarak ulaşmıştır. DEX kriyojelinin MB için yeniden kullanılabilirliği de yapılmıştır. ~30 mg ağırlığındaki DEX kriyojelinin art arda kullanımında, başlangıçta 20 ppm, 30 mL olan MB çözeltisinden absorplanan miktar 6,43±0,15 mg MB/g kriyojel olarak hesaplanmış, bu değer beşinci kullanımdan sonra 4,71±0,48 mg MB/g kriyojel olarak hesaplanmıştır. MB absorplamış DEX kriyojeli ile yapılan salım çalışmalarında ilk kullanımda 3,78±0,33 mg MB/g kriyojel salmıştır, ancak beşinci kullanımdan sonra, salınan miktar, 1 M 30 mL HC1 ile muamele üzerine 0,92±0,38 mg MB/g kriyojel olarak hesaplanmıştır. DEX kriyojelinin MB için adsorpsiyon kinetiği de incelenmiş olunup, 0,9983 korelasyon katsayısı ve 0,36 K_L değeri ile Freundlich, Temkin, Elovich ve Dubinin-Radushkevich izotermleri gibi diğer iyi bilinen modeller arasında en uygun olan Langmuir izoterm modelini temsil ettiği belirlenmiştir.

Anahtar Kelimeler: boya ve pestisit giderimi, dekstran kriyojel, doğal polimer, süper gözenekli/makro gözenekli malzeme

1. Introduction

Dextran (DEX) is a polysaccharide produced from various lactic acid bacteria such as *Leuconostoc mesenteroides*, *Lactobacillus* and *Streptococcus mutans* (Siddiqui et al., 2014; Zafar, et al., 2018; Arriba et al., 2019; Ye et al., 2019). This bacterial exopolysaccharide (EPS) has several advantages over other polysaccharides due to its biodegradable and biocompatible natural properties. Dextran produced by various strains may vary due to the branching type, glyosidic bonds, molecular weight, and physical/chemical properties (Ferreira et al., 2002; Berillo et al. 2012; Wang et al., 2019). Because of its biodegradable, water soluble and biocompatible nature, DEX has been employed in many fields ranging from food industry to cosmetic sector, pharmaceutic and biomedical fields (Levesque et al., 2005; Bölgen et al., 2015; Hotzel and Heinze, 2016; Zhang et al., 2017).

Cryogels, which are three-dimensional polymeric networks with macro or super interconnected pores offering superior physical properties in comparison to conventional hydrogel counterparts of the same materials, are considered notable materials from many aspects (Tripathi et al., 2013; Zhao et al., 2018; Eggermont et al., 2019). As a particular form of hydrogel, cryogel is the polymeric networks that are crosslinked at temperatures below the freezing point of a solvent, while the solvent is generally water (Sahiner et al., 2015; Villard et al., 2019). The characteristics of cryogel such as pore size, elasticity and mechanical strength can be tuned depending on the composition of the precursor solution and the synthesis conditions, such as the amount of solvent used, reaction temperature, cooling rate, concentration of dissolved species e.g., polymer/monomer, crosslinker and accelerator etc. (Orakdogen et al., 2011). Cryogels have superior properties such as fast swelling-shrinkage, high mechanical strength and elasticity (Sengel et al., 2017; Suner et al., 2019; Tavsanli and

Okay., 2020). Because of these innate properties, cryogels are commonly used in biomedical fields including tissue engineering, drug carrier systems, immunotherapy as well as having applications in environmental use such as separation and purification (Sahiner and Demirci, 2016; Sahiner et al., 2017; Topuz and Uyar, 2017; Ciolacu et al., 2016; Hixon et al., 2017; Akilbekova et al., 2018; Guo et al., 2019).

Here, crosslinked superporous cryogels from a natural polymer, DEX, were prepared by means of a cryo-crosslinking method. The swelling behavior of DEX cryogels at different pHs (1-11) was examined and maximum and minimum swelling ratio was determined. In addition, DEX cryogels were demonstrated for use as column fillers for the removal of organic dyes and pesticides from aqueous medium. Furthermore, the MB adsorption kinetics were investigated employing various adsorption models to determine the best isotherm model.

2. Material and Methods

2.1. Materials

Dextran from *Leuconostoc* spp. (DEX, Sigma Aldrich, Mr: 15000-25000 g/mole), and divinyl sulfone (97%, DVS, Sigma-Aldrich) as crosslinker were used as received. For the removal of organic dyes and pesticides from the aqueous medium, methylene blue hydrate (MB, 97%, Sigma-Aldrich) and 1,1′-Dimethyl-4,4′-bipyridinium dichloride (paraquat, PQ, Fluka) were also used as received. Hydrochloric acid (HCl, 36.5-37%, Sigma-Aldrich), sodium hydroxide (NaOH, Merck) and sodium chloride (NaCl, Merck) were used as is. All the aqueous solutions were prepared using distilled water (18.2 M cm from Millipore-Direct Q UV3).

2.2. Synthesis and Characterization of DEX Cryogel

A 5 wt% solution of DEX polymer in 0.2 M NaOH was prepared and then allowed to cool for 3 minutes at -18 °C. Then, 50% of DVS (based on DEX repeating unit) crosslinker was added into the DEX solution and rapidly transferred to pipettes with 6 mm diameter. The pipetted cryogel precursors were left for 24 hours at -18 °C for cryogellation. After 24 h, the obtained solid cryogels were cut into cylindrical shapes and washed with distilled water five times to remove unreacted chemical species. Finally, porous DEX cryogels were dried in a lyophilizer and stored in a closed container for later use.

Morphological analysis of cryogels were done by optical microscopy (Olympus BX53F, Japan) and Field Emission Scanning Electron Microscopy (FE-SEM, Hitachi Regulus 8230). To determine the swelling rate of DEX cryogel in different solution pHs, cryogel pieces weighing about 20 mg were swollen for 1 minute in different solutions in the pH 1-11 range. Then, the surface water was removed from the swollen cryogel by blot-drying with tissue paper and its weight was recorded. The swelling ratios (S%) of DEX cryogels were calculated using equation 1.

$$S\% = [(M_s - M_d) / M_d] \times 100 \quad (1)$$

here, M_s and M_d are the weights of swollen and dry cryogel, respectively.

Potentiometric titration of linear DEX and DEX cryogel was done with 0.1 M NaOH solution as a titrant under nitrogen gas at room temperature. For this purpose, ~ 20 mg of linear DEX and DEX cryogels were placed in two separate beakers containing 40 mL of 0.1 NaCl salt solution and the pH of the solutions containing polymeric structures were set to pH 1 using concentrated HCl and then these solutions were titrated using 0.1 M NaOH solution in the pH range of 1 to 12.

2.3. Methylene Blue and Paraquat Adsorption Studies, Re-Usability and Adsorption Kinetics of DEX Cryogels

About 15 mg DEX cryogel was placed in the glass column and 5 mL of MB in different concentration ranges between 10-150 ppm was passed under gravity. In the same manner, 15 mg of DEX cryogel was placed in a glass column and 5 mL of different concentrations of PQ solution from 5-60 ppm range were passed through the column. The results were determined using UV-Vis spectroscopy (UV-Vis Spec., T80+, PG Instrument Limited) from the calibration curve, constructed for PQ at λ=257 nm (Sahiner et al., 2011). The maximum absorption capacity of DEX cryogel used as column filler was determined by UV-Vis spectroscopy.

Re-use studies were carried out for the adsorption to demonstrate the re-usability of DEX cryogels to remove organic dye such as MB from aqueous media. In the re-use studies, about 30 mg DEX cryogel was placed in a beaker containing 30 mL 20 ppm MB solution for 1 h. Then, the amounts of MB absorbed from the adsorption solution were determined by UV-Vis spectroscopy employing the previously created calibration curve at 664 nm (Xiong et al., 2019). Then, MB which was adsorbed by DEX was removed by treatment with 30 mL 1 M HCl until no MB release was determined by UV-Vis Spectroscopy at 664 nm. Then, these cryogels were washed for 30 min with 30 mL of distilled water, and 1 h with 1 M 30 mL of NaOH, and then again for 30 min with 30 mL of distilled water to remove the acid and base from DEX cryogel for re-generation purposes. Next, the same DEX cryogel was again placed into a beaker containing 30 mL 20 ppm MB dye solution for 1 h for MB adsorption, and these adsorption and release cycles were repeated 5 times to gain information about the re-use of DEX cryogels.

In order to evaluate the adsorption studies in detail, a piece of cryogel weighing about 15 mg was placed into the glass column. MB dye solutions of 5 mL containing 10, 20, 40, 60, 80, 100 and 150 ppm MB were passed through the glass column containing the cryogel via the effect of gravity. The adsorbed amounts of MB were calculated via UV-Vis spectrophotometry from the absorption maximum of MB solution at 664 nm. Various adsorption isotherms were applied to determine the best model to represent MB adsorption onto DEX cryogels.

For the Freundlich isotherm model;

$$\ln q_e = \ln K_F + 1/n \ln C_e \qquad (2)$$

Here, q_e (mg/g) represents the amount of substance adsorbed in equilibrium. C_e (mg/L) is the concentration of the substance remaining in the solution without adsorption, K_F and n are Freundlich isotherm constants.

For the Langmuir isotherm model;

$$C_e/q_e = C_e/q_m + 1/q_m.K_L \qquad (3)$$

Here, q_e (mg/g), is the amount of substance adsorbed by the unit adsorbent, q_m (mg/g), is the maximum amount adsorbed by the adsorbent, C_e (mg/L) is the concentration of the substance remaining in the solution without adsorption, and K_L is Langmuir constant.

For the Temkin isotherm model;

$$q_e = (RT/b) \ln K_T + (RT/b) \ln C_e \quad (4)$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T refers to the temperature in Kelvin, and b is related to adsorption temperature (J/mol). K_T is the Temkin constant.

For the Elovich isotherm model;

$$\ln (q_e/c_e) = \ln (K_E q_m) - (1/q_m) q_e \quad (5)$$

Here, q_e (mg/g), is the amount of substance adsorbed by the unit adsorbent, q_m (mg/g), is the maximum amount adsorbed by the adsorbent, C_e (mg/L) is the concentration of the substance remaining in the solution without adsorption, and K_E is Elovich constant.

For the Dubinin-Radushkevich isotherm model;

$$\ln q_e = \ln q_m - B (RT \ln(1+1/C_e))^2 \quad (6)$$

where q_m represents the adsorption capacity (mg/g). R is the gas constant (8.314 J mol^{-1} K^{-1}), and T refers to the temperature as Kelvin. In addition, ε^2 value is given by $\varepsilon^2 = (RT \ln(1+1/C_e))^2$ equation.

3. Results and Discussion

3.1. Preparation and Characterization of DEX Cryogels

Schematic representation of the synthesis mechanism for the prepared DEX cryogel is shown in Figure 3.1. The ice crystals generated during freezing and cryogellation can serve as pores, and as DEX polymer concentration within ice crystals is increased, the crosslinking can readily take place even though the subzero reaction temperature can reduce the crosslinking rate, and thus super porous or macro porous networks of DEX cryogels can be attained.

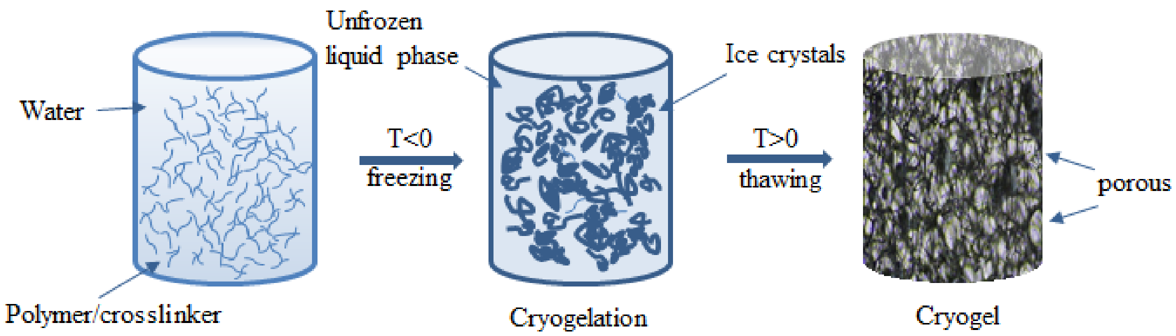

Figure 3.1. Schematic presentation of the synthesis mechanism of DEX cryogel.

The morphological surface properties of the prepared DEX cryogels were imaged using an optical microscope and SEM images. Optical microscope images of the dry and DI water swollen DEX cryogels and SEM images of dry DEX cryogels are given in Figure 3.2.

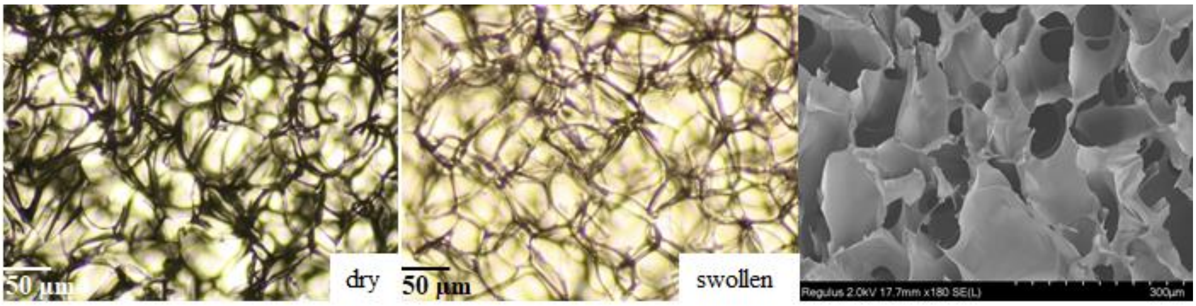

Figure 3.2. Dry and water swollen optical microscope and SEM images of DEX cryogels.

In the dry cryogel sample the pores are in the form of intertwined nets. The pores are enlarged by swelling of the cryogel. The optical microscope and FE-SEM images in Figure 3.2 reveal that the pore sizes of DEX cryogels are in the range of about 50-300 µm.

The swelling behavior of DEX cryogels in the range of pH 1 to 11 was examined using about 20 mg of dry cryogel in 10 mL of different pH solutions. The pH of the solutions was adjusted using 0.1 M NaOH and 0.1 M HCl solutions. The swelling ratio% (S%) of DEX cryogels was calculated by using equation 1. The swelling behavior of DEX cryogels at different pHs, 1-11 are given in Figure 3.3 (a). As can be seen from Figure 3.3 (a), S% value of DEX cryogel slowly decreased between pH 1 and 5, and then increased from pH 5 to 11. DEX cryogels displayed maximum swelling behavior at pH 11 with a S% value of 1516±90% because of the abundant number of acidic hydroxyl (OH) groups that can dissociate under basic solution pHs. DEX cryogel also showed minimum swelling behavior with S% value of 1168±42% at pH 5.

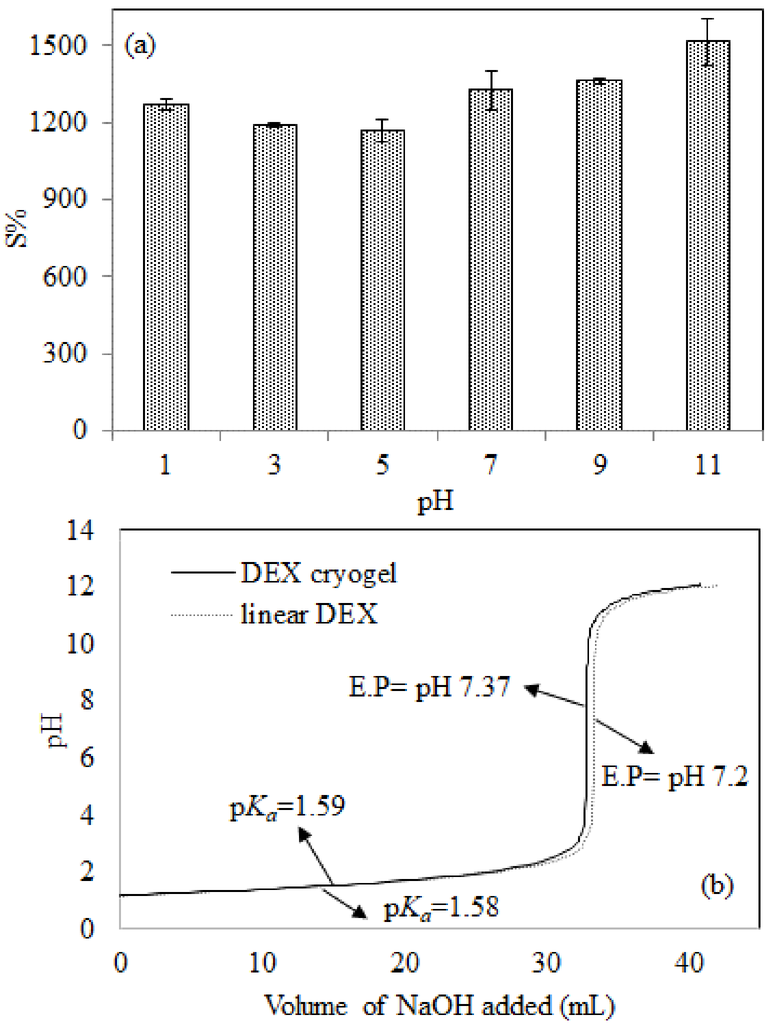

Figure 3.3. (a) Swelling behavior of DEX cryogels in different solution pHs in the 1-11 range, and (b) potentiometric titration curves of linear DEX and DEX cryogels titrated with 0.1 M NaOH and their equivalence point (EP) and p*Ka* values.

To investigate the effect of crosslinking mechanism on the functional groups of DEX, potentiometric titration of linear DEX and DEX cryogels was performed, and the corresponding graphs are shown in Figure 3.3 (b). From the titration of linear DEX and DEX cryogel curves, the equivalence points (EP) were determined as pH 7.2 and pH 7.37, respectively. The pH of the volume corresponding to the half-equivalence point is generally considered to be the pK_a value of the materials. Therefore, linear DEX and DEX cryogels have pK_a values of 1.59 and 1.58 which are very close to each other. Consequently, it can be assumed that crosslinking slightly alters, e.g., lowers the pK_a value of linear DEX upon crosslinking as the highly crosslinked structure somehow hinders the dissociation of the acidic groups reducing the pK_a values.

3.2. The use of DEX Cryogels for Methylene Blue (MB) and Paraquat (PQ) Adsorption

The adsorption of MB and PQ by DEX cryogels was performed by placing about 15 mg of DEX cryogel into a glass column and passing 5 mL of MB or PQ solutions through the column under the influence of gravity. The UV-Vis spectra of the MB and PQ solutions upon adsorption by DEX cryogel within the column were examined using constructed calibration curves at 664 and 257 nm, respectively. The maximum adsorption amounts for MB and PQ were determined from adsorption amount versus concentration graphs for each organic species as shown in Figure 3.4 (a) and (b), respectively. Whether MB or PQ, 5 mL volume with different concentrations were passed through the column containing DEX cryogel until a maximum adsorption amount was attained and their adsorbed amount versus concentration for MB or PQ curves were constructed as illustrated in Figure 3.4 (a) and (b), respectively. It is apparent that DEX cryogel reached its maximum absorption capacity by adsorbing 10.69±0.14 mg MB/g DEX. On the other hand, the maximum amount of PQ adsorbed was determined as 2.87±0.33 mg PQ/g DEX. As higher amounts of adsorption were accomplished by MB among the adsorbates, the re-usability studies and adsorption isotherm studies were only done for MB.

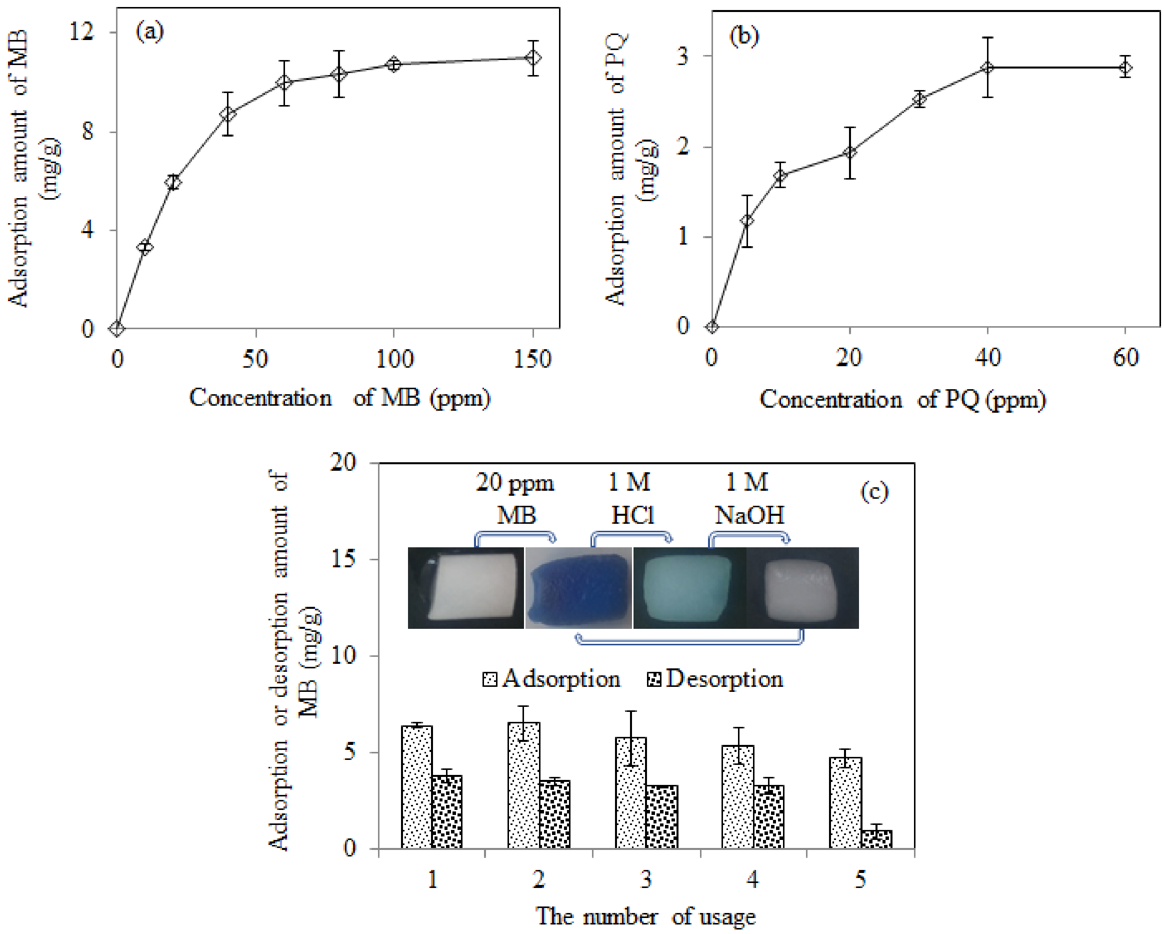

Figure 3.4. The adsorption capacity of DEX cryogels for (a) MB, (b) PQ, and (c) adsorption and desorption studies of MB from DEX cryogels [Reaction conditions: 30 mg DEX cryogel, 30 mL 20 ppm MB dye solution].

To demonstrate the re-usability of DEX cryogels as column filler material, ~30 mg DEX cryogel and 30 mL 20 ppm MB dye solution were put in a beaker. After MB adsorption, the MB-adsorbed DEX cryogel was treated with 30 mL 1 M HCl for 1 h and washed with distilled water for 30 min. Then it was treated with 1 M NaOH solution for 1 hour and washed with distilled water for 30 min. Thus, the adsorbed dye was removed from the cryogel which was re-used by placing this re-generated DEX cryogel in 30 mL of 20 ppm dye solution. By repeating the same procedure five times, graphs were prepared for adsorption and desorption amount of MB versus the number of uses along with digital camera images and are illustrated in Figure 3.4 (c). It is clear that the initial amount of adsorption was 6.43±0.15 mg/g and this amount gradually reduced and after the fifth use it decreased to 4.71±0.48 mg/g. Parallel to the adsorption behavior, the initial desorbed amount was calculated as 3.78±0.33 mg/g and this value reduced to 0.92±0.38 mg/g after the fifth use suggesting that during every use a slight capacity reduction is observed for both adsorption and desorption. This could be explained by the fact that DEX cryogel is degradable and there maybe loss of DEX moieties from the cryogel structure during every cycle. Overall, these results reveal that DEX cryogels are suitable benign material for removal or separation of toxic species such as dyes and pesticides from aqueous environments.

3.2. Adsorption Isotherms

Adsorption phenomena continues until equilibrium is reached between the amount of substance held per unit weight or surface area of adsorbent and the concentration of substance remaining in solution at constant temperature. This is explained mathematically by adsorption isotherms. Adsorption of MB from aqueous solutions was carried out at seven different concentrations, 10, 20, 40, 60, 80, 100 and 150 ppm each in 5 ml. Using ~15 mg of DEX cryogel in a glass column, these dye solutions were passed through the column by contacting with DEX cryogels. The adsorption amounts were calculated for MB from the previously constructed calibration curve using UV-Vis spectrophotometer at a wavelength of 664 nm.
Five different isotherm models were applied to determine the nature of adsorption of MB into DEX cryogels. The most commonly used isotherm models of Langmuir, Freundlich, Temkin, Elovich and Dubinin-Radushkevich were used to determine the best fit for the adsorption phenomena. The isotherm models applied for MB into DEX cryogels are given in Figure 3.5, using equations 2, 3, 4, 5 and 6, respectively.

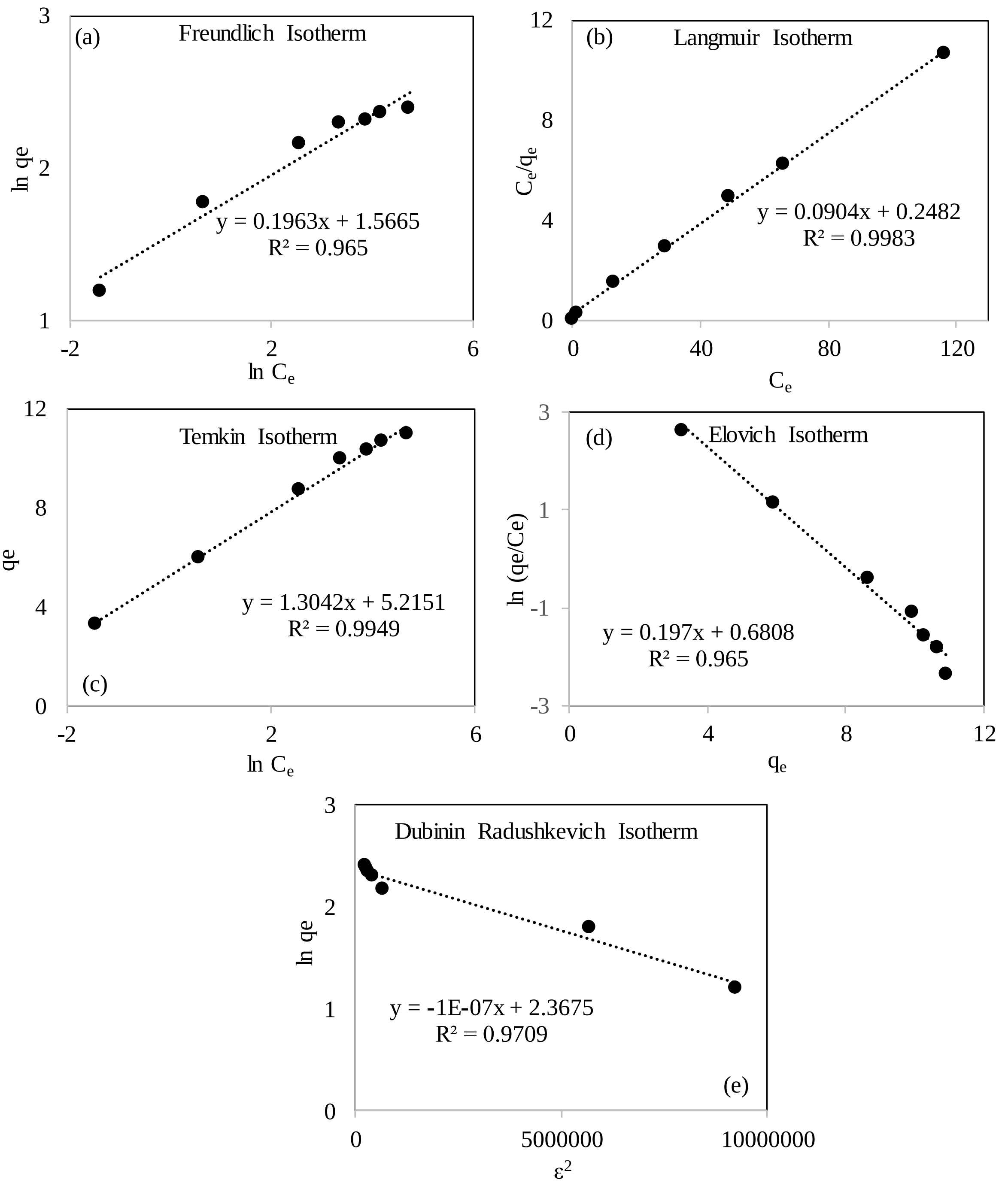

Figure 3.5. MB dye adsorption into 50% DVS crosslinked DEX cryogels by applying (a) Freundlich, (b) Langmuir, (c) Temkin, (d) Elovich and (e) Dubinin Radushkevich isotherm models.

The corresponding isotherm constant and correlation constants for each of the used isotherm models are given in Table 3.1. As can be clearly seen from the correlation coefficients, the highest value of R^2=0.9983 for MB adsorption is obtained for the Langmuir isotherm model.

Table 3.1. Isotherm constants for the adsorption of MB onto DEX cryogels.

Freundlich		Langmiur		Temkin		Elovich		Dubinin Radushkevich	
K_F (L/g)	4.78	K_L (L/g)	0.36	K_T (L/g)	54.52	K_E (L/g)	0.39	B	0.99
R^2	0.965	R^2	0.9983	R^2	0.9949	R^2	0.965	R^2	0.9709
n	5.09	q_m (mg/g)	11.06	b	1899.7	q_m (mg/g)	5.08	q_m (mg/g)	10.67

In the Langmuir isotherm model, the surface is covered with a monolayer of adsorbate at the maximum saturation point, and it is assumed that the adsorbed surface is homogeneous. In the Freundlich isotherm, the adsorption areas on the adsorbent surface are heterogeneous. The Temkin isotherm is derived by assuming that the decrease in adsorption energy is linear. The Elovich isotherm on the other hand was created for the chemical adsorption of gases onto solid surfaces and explains that the adsorption rate decreases exponentially as gas adsorption increases. The Dubinin-Radushkevich isotherm also provides information about whether the adsorption on the heterogeneous surface occurs chemically or physically (Hamdaoui and Nafferechoux, 2007; Fil et al. 2014; Habeeb et al. 2017). Therefore, from Figure 3.5 and Table 3.1, it can be assumed that the adsorption of MB can fit all five isotherm models; however, it is best fitted to the Langmuir isotherm model because of the highest correlation coefficient, 0.9983. Isotherm types for Langmuir indicate that if $K_L>1$, $K_L= 1$, $0<K_L<1$ and $K_L= 0$, adsorption is expressed as unfavorable, linear, spontaneous and irreversible, respectively. In this case, as can be seen from Table 3.1, for the Langmuir isotherm, K_L has a value of 0.36 suggesting a spontaneous adsorption process.

4. Conclusion

It was shown here that toxic and harmful organic substances such as organic dyes and pesticides can be readily removed from aqueous environments using natural polymeric super-porous structures. The cryogel based on DEX was shown to be capable of removing MB in about seven minutes at 10.69±0.14 mg/g and PQ at 2.87±0.33 mg/g in about ten minutes. The re-usability and re-generatability of DEX cryogels further corroborate the viable potential environmental applications of this natural polymer-based structure for the removal and/or separation of toxic species. Amongst isotherms applied for MB adsorption into DEX cryogel, the Langmuir isotherm was found to have the best fit with R^2 value of 0.9983. It is also noteworthy to mention that DEX is biodegradable and can be obtained from natural sources without causing any impairment to the environment so it is expected to become prevalent, and is a promising material for future applications in environmental and biomedical fields.

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