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Tetracycline adsorption via dye-attached polymeric microbeads

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Abstract

In this study, the adsorption of tetracycline (TC) onto polymeric microbeads was investigated. For this purpose, suspension polymerization was used to synthesize poly(2-hydroxyethyl methacrylate) [poly(HEMA)] microbeads. Cibacron Blue F3GA (CB) was covalently attached to poly(HEMA) microbeads and the microbeads were tested as an adsorbent for subsequent TC adsorption. The effects of various parameters, such as pH value, initial TC concentration, temperature, and contact time, were investigated. The maximum adsorption capacity (Q) of microbeads was found to be 9.63 mg g^{-1} at pH 7.0. The results showed that the adsorption process was fast and occurred spontaneously within the first 5 minute. The adsorption process was fitted to the Freundlich isotherm model. The thermodynamic parameters of the adsorption, the enthalpy ($\Delta H°$) and entropy ($\Delta S°$), were calculated as 69.26 kJ mol^{-1} and 0.290 kJ mol^{-1} K^{-1}, respectively. The Gibbs free energy ($\Delta G°$) was also calculated in the range of -11.069 kJ mol^{-1} to -17.159 kJ mol^{-1} with increase in temperature from 277 K to 298 K indicating that the TC adsorption process was spontaneous and endothermic. The results revealed that the poly(HEMA) microbeads could be effectively used to adsorption of TC from aqueous solution.

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1. Introduction

Antibiotics are widely used to cure pathogenic or bacterial diseases in animals and humans [1]. Besides, they are also used as feed additives in aquaculture and the poultry industry to promote animal growth [2]. Since most antibiotics are difficult to metabolize, a large fraction of ingested antibiotics is excreted in feces or urine into the environment [3] and pollutes soil [4] and water sources [5].

Tetracyclines (TCs), which comprise oxytetracycline (OTC), chlortetracycline (CTC), and tetracycline (TC), are commonly used antibiotics worldwide [6]. TC is an aromatic polyketide product of the biosynthetic pathway with poor absorption, low metabolism and overexploitation. Thus, the environmental pollution by TC residues affects human health and aquatic ecosystems [7].

At present, there are various technologies to remove TC from water, like coagulation [8], photocatalytic degradation [9], electrochemical processes [10], ion exchange [11], filtration [12], biological processes [13], sedimentation [14], ozonation [15], and adsorption [16]. Among these, adsorption is an attractive and effective process [17] due to its removal efficiency, safety, low-cost adsorbents, and easy operation [18]. Furthermore, various adsorbents, such as biological sludge [19], cryogels [20], activated carbons [21], metal oxides [22], chitosan [23], and polymers [24], are used to remove TCs.

Reactive dyes are often used as affinity ligands for the adsorption or separation of proteins, enzymes and heavy metals. In addition, they are effective and can easily be attached to the carrier matrix. Cibacron Blue F3GA (CB) is a monochlorotriazine dye containing four amino and three sulfonate groups and has been used as an affinity ligand in various biotechnological studies [25].

In the present study, poly(2-hydroxyethyl methacrylate) [poly(HEMA)] microbeads were synthesized via suspension polymerization, and CB was covalently attached onto microbeads. Poly(HEMA)-CB microbeads were characterized by Fourier transform-infrared spectroscopy (FT-IR), elemental analysis, and scanning electron microscopy (SEM). Then, the effects of pH, initial TC concentration, temperature, and contact time on the TC adsorption onto poly(HEMA)-CB microbeads were examined. Furthermore, the adsorption mechanism, adsorption isotherms and kinetic parameters of TC adsorption were evaluated, and the thermodynamic parameters were also calculated and discussed.

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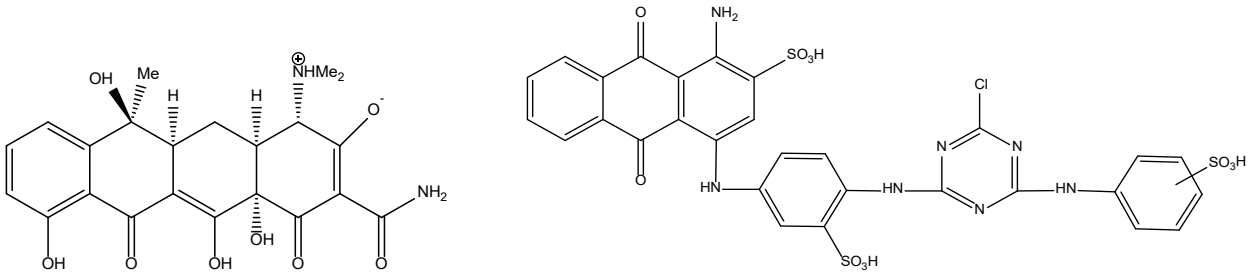
2. Materials and Methods

2.1. Materials

2-hydroxyethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EGDMA) were obtained from Fluka. 2,2'-azobisisobutyronitrile (AIBN), toluene, NaOH and ethylene glycol were obtained from Merck. Cibacron Blue F3GA (CB), tetracycline (TC), poly(vinyl alcohol) (PVA), CH_3COOH, CH_3COONa, NaH_2PO_4, Na_2HPO_4 and KNO_3 were purchased from Sigma. The chemical structures of TC and CB were given in Figure 1.



(a) **(b)**

Figure 1. The chemical structures of **(a)** TC and **(b)** CB

2.2. Preparation of poly(HEMA) microbeads

Poly(HEMA) microbeads were prepared by suspension polymerization in aqueous media [26]. Ethylene glycol dimethacrylate (EGDMA, 4 mL) and 2-hydroxyethyl methacrylate (HEMA, 4 mL) were used as comonomers and mixed with toluene (4 mL) to prepare the organic phase. First, 0.2 g poly(vinyl alcohol) (PVA) was dissolved in 50 mL distilled water to prepare the dispersion medium. Then, 0.1 g of 2,2'-azobisisobutyronitrile (AIBN) was dissolved in the monomer phase which was used as the polymerization initiator. The mixture was poured into a glass polymerization reactor (100 mL) and then, stirred magnetically at 400 rpm. The polymerization was performed at 65 °C for 4 h and at 80 °C for 2 h. After polymerization, the poly(HEMA) microbeads were washed with distilled water and ethanol several times to remove residuals.

2.3. Cibacron Blue F3GA attachment to poly(HEMA) microbeads

Poly(HEMA) microbeads (3.0 g) were magnetically stirred (400 rpm) with CB aqueous solution (3.5 mg/mL, 100 mL) which was containing NaOH (4.0 g) at 80 °C for 4 h [26]. After incubation, CB-attached microbeads were filtered and for removing unattached CB, washed with ethanol and distilled water several times.

2.4. Characterization studies

To identify the morphology of the microbeads SEM (ZEISS EVO 40, Carl Zeiss AG, Germany) was used. FTIR spectrophotometer was used to characterized the poly(HEMA) microbeads, CB and CB-modified poly(HEMA) (poly(HEMA)-CB) microbeads (Perkin Elmer, Spectrum 100, USA).

Elemental analysis was performed to determine the amount of CB attached to the poly(HEMA) microbeads (Leco Elemental Analyzer, CHNS-932, St. Joseph, MI).

The size distribution and average size of the microbeads were detected by screen analysis performed with Tyler standard sieves (Retsch Gmb & Co., KG, Haan, Germany).

2.5. Adsorption studies

Adsorption studies were performed in a batch system containing 20 mL of TC solution and 0.02 g poly(HEMA)-CB microbeads. To detect the effect of the pH of the medium on the adsorption capacity (Q) of the poly(HEMA)-CB microbeads, TC solutions with various pH values (in the range of 3.0 to 9.0, 10 mg L^{-1}, 20 mL) were prepared using acetate or phosphate buffer (0.1 M). The microbeads were stirred magnetically at 200 rpm at 25 °C. In the concentration range of 1.0 mg L^{-1} to 50.0 mg L^{-1}, the TC solutions were prepared at pH 7.0 to investigate the effect of the initial TC concentration on the Q of the poly(HEMA)-CB microbeads at 4 °C, 12 °C and 25 °C (20 mL, 200 rpm). After the adsorption of TC onto poly(HEMA)-CB microbeads, the suspensions were centrifuged (Allegra 64R, Beckman Coulter) at 10,000 rpm for 10 min. The concentrations of the initial and final TC solutions were measured spectrophotometrically at 358 nm (Shimadzu-2100 UV-vis spectrophotometer). All batch studies were performed in triplicate. The amount of adsorbed TC was calculated as follows:

$$Q = \frac{(C_0 - C_e)\,V}{m} \quad (1)$$

where Q (mg g^{-1}) is the adsorption capacity, C_0 and C_e (mg L^{-1}) are the initial and final concentrations of the solution, respectively, V (L) is the volume of the initial solution, and m (g) is the adsorbent weight.

2.6. Desorption and repeated studies

To specify the performance of the adsorbent, adsorption-desorption cycles were performed five times by using the same microbeads. The initial TC concentration of the solution was 5 mg L^{-1} and the final volume was 20 mL at 25 °C. KNO_3 (1 M) solution, ethylene glycol (10 %, w/w %) solution and KNO_3:ethylene glycol (1:1; 1 M:10 %) mixture were used as desorption agents. The total volume of the desorption agents was 20 mL and was stirred magnetically (200 rpm) at 25 °C. The final TC solutions were measured spectrophotometrically. The desorption ratio was calculated as follows:

$$Desorption\ Ratio = \frac{amount\ of\ TC\ desorbed}{amount\ of\ TC\ adsorbed} \times 100 \quad (2)$$

3. Results and Discussion

3.1. Characterization of the poly(HEMA)-CB microbeads

The surface morphology was determined by SEM analyses (Figure 2). The SEM images reveal that the beads were homogeneous and spherical with a rough surface and a diameter in the range of 106 to 300 μm.

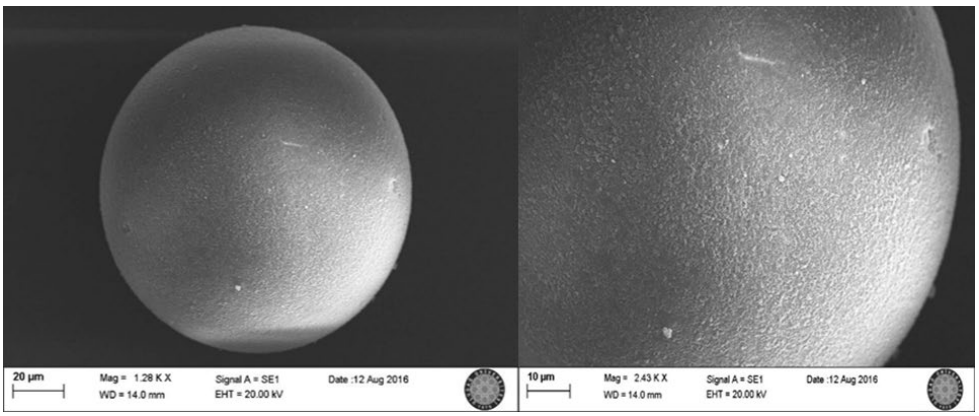


Figure 2. SEM images of poly(HEMA) microbeads

According to the nitrogen stoichiometry determined by elemental analysis, the amount of attached CB to poly(HEMA) microbeads was 10.44 mg CB/g microbeads [26].

To examine the interaction between the poly(HEMA) microbeads and CB, the FTIR spectra of poly(HEMA) microbeads, CB and poly(HEMA)-CB microbeads were achieved (Figure 3). The FTIR spectrum of poly(HEMA) microbeads exhibited a characteristic O-H stretching vibration band at 3200-3600 cm^{-1}. The C-H stretching band of CH_3, the C=O stretching band, and the C-O ester stretching vibration band were observed at 2948 cm^{-1}, 1716 cm^{-1}, and 1247 cm^{-1}, respectively. The C-Cl stretching band at 1087 cm^{-1} and the S-O stretching vibration band at 1042 cm^{-1} and 1022 cm^{-1}, respectively, appeared in the FTIR spectrum of CB. In the FTIR spectrum of poly(HEMA)-CB microbeads, the characteristic O-H stretching vibration band appeared as a broad peak at 3200-3600 cm^{-1}. Due to the dye attachment to the polymer, some additional absorption bands that differed from poly(HEMA) microbeads were observed in the spectrum of poly(HEMA)-CB microbeads. The bands at 1022 cm^{-1}, 1073 cm^{-1}, and 1154 cm^{-1} can be attributed to the stretching vibration of S-O, the symmetric stretching of S=O, and the asymmetric stretching of S=O, respectively, and are a result of the CB attachment to poly(HEMA) microbeads. Additionally, vibrations of the primary and secondary amine groups of CB were observed at 849 cm^{-1} and 897 cm^{-1}. At 1534 cm^{-1}, N-H bending was determined as a broad band. This result shows that CB was successfully attached to poly(HEMA) microbeads [26-28].

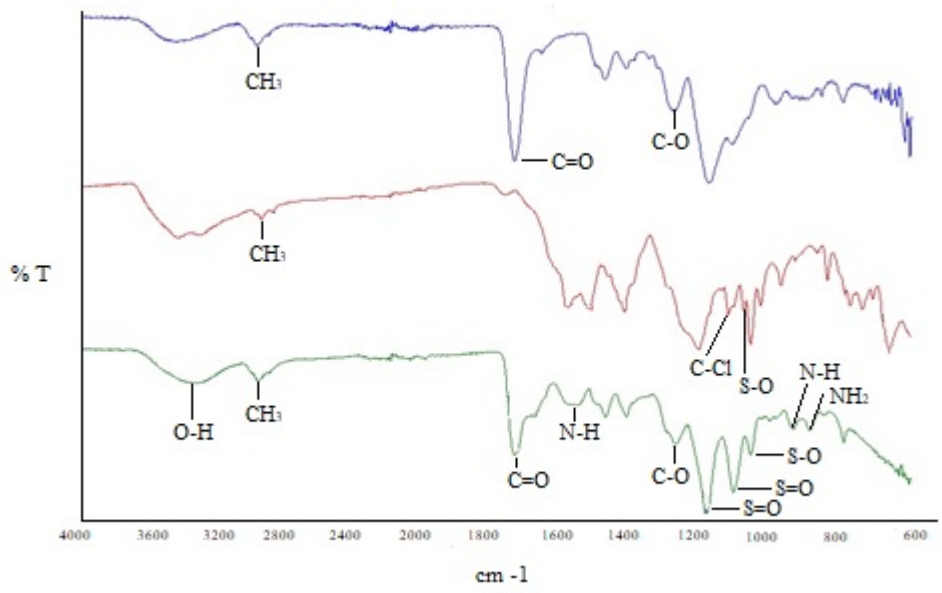


Figure 3. FTIR spectra of poly(HEMA)-CB (green), CB (red), and poly(HEMA) (blue)

3.2. Effect of pH value on TC adsorption

One of the most important parameter in an adsorption proceses is the initial pH value of the solution. To identify the effect of the pH on the TC adsorption on poly(HEMA)-CB microbeads, 10 mg L^{-1} TC solution was prepared at various pH values ranging from 3.0 to 9.0 (Figure 4). TC exhibits ionizable and polar groups such as amino, phenol, ketone, carboxyl and alcohol groups. It has three dissociation constants, and under acidic, partially acidic to neutral, and alkaline conditions, it appears as cationic species (pKa = 3.3), zwitterionic species (pKa = 7.68) and anionic species (pKa = 9.7), respectively [29]. Due to the amphoteric character of TC, the initial pH value of the aqueous solution can easily affect both the protonation of the TC molecule and the physicochemical properties of the adsorbent [30]. CB (pKa = 0.78), a monochlorotriazine dye, contains four basic primary and secondary amino groups and three sulfonic acid groups that affect ionic and hydrophobic interactions. CB dye molecules were covalently attached to the poly(HEMA) microbeads via the hydroxyl groups of the polymer and the reactive triazine ring of the dye [31]. The adsorption capacity of poly(HEMA)-CB for TC increased in the pH ranging from 4.0 to 7.0 and dramatically decreased for pH values higher than 8.0. These results could be caused by repulsive electrostatic forces between TC and the CB dye. *Q* was observed as 1.17 mg g^{-1} at pH 7.0. Specific interactions, such as hydrogen bonding and electrostatic and hydrophobic interactions between poly(HEMA)-CB microbeads and TC, may result from the ionization states of the dye (i.e., sulfonic acid and amino) and TC (i.e., amino) at pH 7.0. In Figure 5, possible interactions between poly(HEMA)-CB and TC are also given.

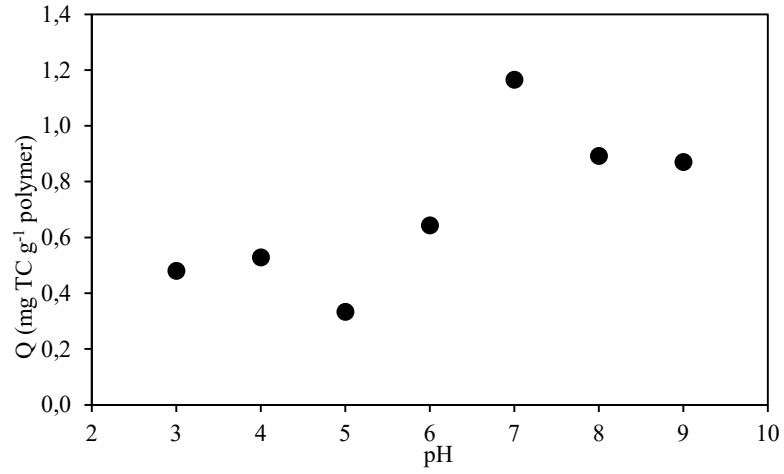


Figure 4. Effect of the pH on TC adsorption (C_{TC} = 10 mg/L; T = 25 °C; $m_{poly(HEMA)-CB}$ = 0.02 g; V = 20 mL)

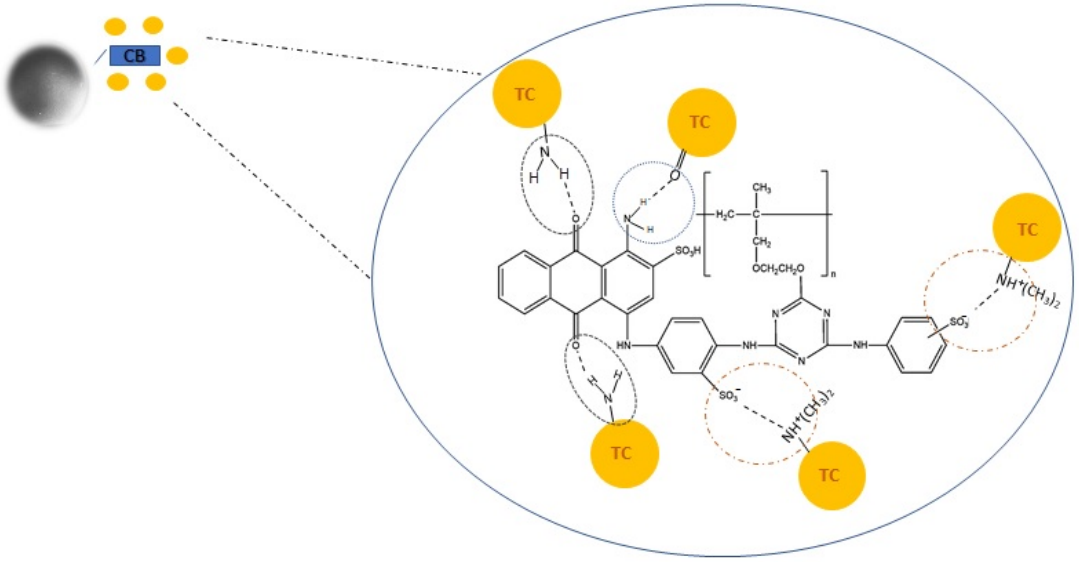


Figure 5. Schematic representation of possible interactions between poly(HEMA)-CB and TC

3.3. Effects of initial concentration and contact time on TC adsorption

Figure 6 shows the effect of the initial TC concentration on the adsorption at various temperatures (4 °C, 12 °C and 25 °C). The adsorption process was carried out for 24 hours. The adsorption capacity increased from 0.121 mg g^{-1} to 5.159 mg g^{-1} and from 0.686 mg g^{-1} to 9.627 mg g^{-1} after increasing the initial TC concentration from 1 mg L^{-1} to 50 mg L^{-1} at 12 °C and 25 °C, respectively. The maximum adsorption capacity did not change dramatically at 4 °.

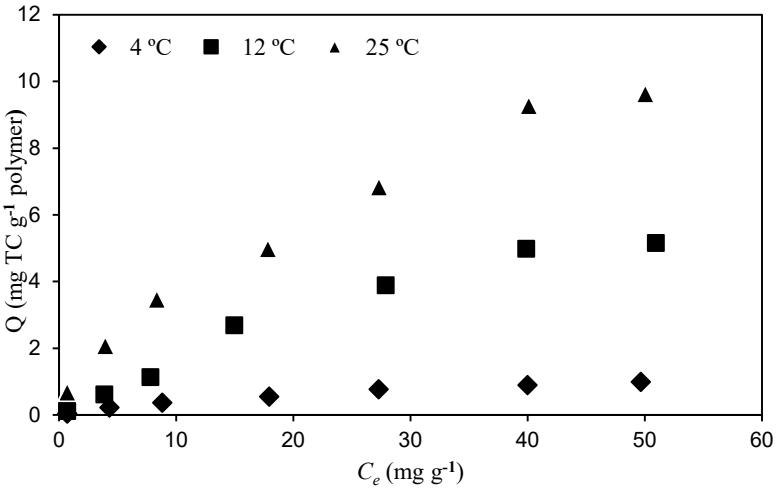


Figure 6. Effect of the initial TC concentration on adsorption at different temperatures (C_{TC} = 1-50 mg/L; $m_{poly(HEMA)-CB}$ = 0.02 g; V = 20 mL)

To develop an effective and applicable adsorption process, it should be performed in a short time [32]. To determine the TC adsorption performance over time, the adsorption process was performed at different contact times ranging from 5 min to 60 min at various temperatures (4 °C, 12 °C and 25 °C). TC adsorption occurred quickly within the first 5 min and continued for 60 min with no remarkable change after 60 min. The adsorption capacities for 10 mg L^{-1} initial concentration of TC were calculated as 1.323 mg g^{-1}, 1.985 mg g^{-1} and 3.415 mg g^{-1} at 4 °C, 12 °C and 25 °C, respectively (Figure 7). The adsorption of TC onto poly(HEMA)-CB microbeads occurred at a fast rate; therefore, the kinetic parameters could not be calculated.

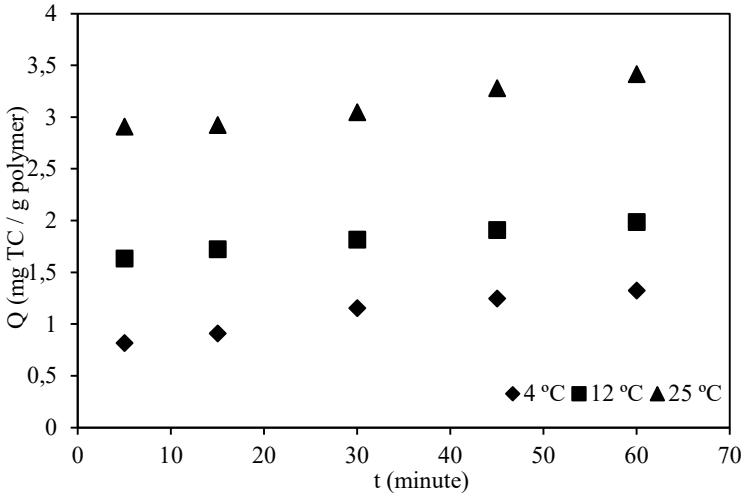


Figure 7. Effect of contact time on TC adsorption (C_{TC} = 10 mg/L; $m_{poly(HEMA)-CB}$ = 0.02 g; V = 20 mL)

3.4. Adsorption isotherms

Isothermal analysis was also performed to investigate the adsorption capacity of poly(HEMA)-CB microbeads for TC. The Langmuir (Eq. 3), Freundlich (Eq. 4) and Dubinin-Raduskhevich (D-R) (Eq. 4) isotherm models were applied to analyze the adsorption process of poly(HEMA)-CB microbeads at 277, 285 and 298 K (Figure SI 1-Figure SI 9).

The Langmuir isotherm model is defined as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_L K_L} + \frac{C_e}{Q_L} \quad (3)$$

where C_e (mg L^{-1}) is the concentration of the adsorbate in solution at equilibrium, Q_L (mg g^{-1}) is the maximum adsorbate uptake, q_e (mg g^{-1}) is the adsorbate uptake at equilibrium, and K_L (L mg^{-1}) is the Langmuir adsorption equilibrium constant [33].

The Freundlich isotherm model is defined as follows:

$$lnq_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

where C_e (mg L^{-1}) is the concentration of the adsorbate in solution at equilibrium, K_F (mg g^{-1}) is the Freundlich adsorption equilibrium constant, n is the Freundlich linearity index, and q_e (mg g^{-1}) is the adsorbate uptake at equilibrium [34].

The Langmuir and Freundlich parameters were determined by the MATLAB package program. The adjusted R^2 (R^2_{adj}) and standard deviation (SD) of the obtained models were calculated. The adsorption isotherms of TC for various temperatures are given in Table 1.

The Dubinin-Radushkevich isotherm model is defined as follows:

$$\ln Q_e = \ln Q_{D-R} - K_{D-R}\varepsilon^2 \quad (5)$$

where Q_e (mg g^{-1}) is the amount of adsorbed solute, K_{D-R} (mol^2 J^{-2}) is the D-R constant, and Q_{D-R} (mg g^{-1}) is the maximum adsorption capacity. ε is the Polanyi potential (J mol^{-1}) and can be defined as:

$$\varepsilon = RTln\left(1 + \frac{1}{C_e}\right) \quad (6)$$

where R (J mol^{-1} K^{-1}) is the gas constant, C_e (mg L^{-1}) is the equilibrium concentration of the adsorbate, and T (K) is the temperature [35]. K_{D-R} values were used to calculate the free energy of adsorption (E_{fe}) (Eq. 7):

$$E_{fe} = \frac{1}{\sqrt{-2K_{D-R}}} \quad (7)$$

The Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were used to fit the experimental data. The Langmuir isotherm model describes adsorption processes on a homogeneous surface. The Freundlich model can be applied to multilayer adsorption with a nonuniform distribution over a heterogeneous surface [34]. In the present study, the Freundlich model (R^2 > 0.9647, R^2_{adj} > 0.9576) and the Langmuir model (R^2 > 0.9823, R^2_{adj} > 0.9787) were fitted to adsorption data with high correlation coefficients (Table 1).

Table 1. Parameters of adsorption isotherms of TC onto poly(HEMA)-CB at different temperatures

Isotherm Model	Parameter	Temperature (K)		
		277	285	298
Langmuir	Q_{exp} (mg g^{-1})	0.989	5.158	9.620
	Q_L (mg g^{-1})	1.565	9.676	16.880
	K_L x 10^3 (L mg^{-1})	33.830	24.400	27.090
	R^2	0.9965	0.9823	0.9848
	R^2_{adj}	0.9958	0.9787	0.9818
	SD	0.0229	0.3049	0.4675
Freundlich	K_F (mg g^{-1}) (L $mg^{-1})^{1/n}$	0.1013	0.3897	0.899
	N	1.693	1.478	1.626
	R^2	0.9931	0.9647	0.9906
	R^2_{adj}	0.9917	0.9576	0.9906
	SD	0.0323	0.4303	0.3356
D-R	Q_{exp} (mg g^{-1})	0.989	5.158	9.620
	Q_{D-R} (mg g^{-1})	0.536	4.230	7.120
	K_{D-R} (mol^2 J^{-2})	6.13 x 10^{-7}	7.14 x 10^{-6}	2.01 x 10^{-5}
	E (kJ mol^{-1})	0.902	0.264	0.160
	R^2	0.8239	0.8004	0.8903

In Langmuir model in spite of high values of R^2 and R^2_{adj}, Q_{exp} values are not close to Q_L values at all studied temperatures. According to the results, $1/n < 1$, where $1/n$ is a heterogeneity parameter, fit the Freundlich isotherm model.

The Dubinin-Radushkevich isotherm model, which is a pore-filling model, is generally applied to explain the adsorption mechanism onto a heterogeneous surface with a Gaussian energy distribution, and it is temperature-dependent [35]. The values of the free energy of adsorption (E_{fe}) were 0.902 kJ mol^{-1}, 0.264 kJ mol^{-1} and 0.160 kJ mol^{-1} for 277 K, 285 K and 298 K, respectively. D-R model is used to determine the nature of the adsorption prosesess as whether chemical ($8 < E_{fe} < 16$ kJ mol^{-1}) or physical (< 8 kJ mol^{-1}). The results show that the adsorption of TC onto poly(HEMA)-CB microbeads was a physical process.

Numerous adsorbents were used for TC adsorption, and the comparative results of some adsorption capacities for different adsorbents are shown in Table 2. The adsorption capacity of poly(HEMA)-CB is comparable with other adsorbents which have been used in TC removal from aqueous solutions. As can be seen in Table 2, poly(HEMA)-CB has the second best performance. The size and shape of adsorbents also have an important role in adsorption process. It effects the adsorption capacity. Also, the physical composition of adsorbent can be easily controlled in the polymerization compared to given methods used to prepare biochars.

Table 2. Comparative results of different adsorbents for TC adsorption.

Adsorbent	pH	q_e (mg g^{-1})	Time (min)	Adsorption isotherm	Reference
Magnetic chitosan	6.0	14.34	120	Freundlich	[36]
Rice husk ash	5.0	8.37	600	Langmuir	[37]
Biochar	6.0	5.26	1440	Freundlich	[38]
Microplastics	-	0.12	1440	Linear	[39]
Poly(HEMA)-CB microbeads	7.0	9.63	1440	Freundlich	This study

3.5. Thermodynamic parameters

Thermodynamic parameters play an important role in predicting the adsorption mechanism, whether it is a chemical or physical process. Thermodynamic parameters (i.e., enthalpy ($\Delta H°$), the Gibbs free energy ($\Delta G°$), and entropy ($\Delta S°$)) explain the spontaneity and feasibility of an adsorption process, and are directly dependent on the equilibrium constant between two phases. Generally, the van't Hoff equation is used to determine the thermodynamic parameters:

$$\ln K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \quad (8)$$

where R (8.314 J mol^{-1} K^{-1}) is the universal gas constant, and K is the equilibrium constant, and T (K) is the temperature.

The values of $\Delta G°$ (kJ mol^{-1}) were calculated from the K values for each temperature, and the values of $\Delta S°$ (kJ mol^{-1} K^{-1}) and $\Delta H°$ (kJ mol^{-1}) were calculated from the intercept and slope of the plot of ln K versus 1/T, respectively. $\Delta G°$ can be calculated as:

$$\Delta G° = \Delta H° - T\Delta S° \quad (9)$$

From Eq. 9, $\Delta G°$ was calculated as -11.069 kJ mol^{-1}, -13.389 kJ mol^{-1} and -17.159 kJ mol^{-1} at 277 K, 285 K and 298 K, respectively. The negative value of $\Delta G°$ indicates a spontaneous adsorption process. In addition, more negative values of $\Delta G°$ with increasing temperature suggest that the adsorption is more favorable at higher temperatures [40]. From the van't Hoff equation, $\Delta S°$ and $\Delta H°$ were calculated as 0.290 kJ mol^{-1} K^{-1} and 69.26 kJ mol^{-1}, respectively. These results indicate that the reaction is endothermic with an increased randomness of the adsorbent-liquid interface during TC adsorption onto the active sites of poly(HEMA)-CB microbeads and that this adsorption process is possible and occurs spontaneously.

3.6. Desorption studies

Desorption studies indicate that KNO_3:ethylene glycol (1:1; 1 M:10 %) mixture was more efficient than KNO_3 (1 M) solution or ethylene glycol (10 %, w/w %) solution in desorbing TC. The desorption efficiency of KNO_3:ethylene glycol mixture, KNO_3 solution and ethylene glycol solution was calculated as 94.87 %, 78.38 %, and 55.55 %, respectively. To examine the reusability of the microbeads, five adsorption-desorption cycles were conducted, and it was found that the Q decreased from 9.63 mg g^{-1} to 8.97 mg g^{-1} (6.85 %) during an adsorption-desorption cycle. The results showed that the adsorbent can be used repeatedly without losing efficiency.

3.7. Comparison of poly(HEMA) and poly(HEMA)-CB microbeads

To examine the efficiency of TC adsorption onto CB-attached poly(HEMA) microbeads, TC adsorption experiments were performed with both of the microbeads. TC adsorption was performed for 24 h at 25 °C with a total solution volume of 20 mL. According to the results, for a 50 mg L^{-1} initial TC concentration, the maximum adsorption capacities of TC on poly(HEMA) and poly(HEMA)-CB were calculated as 2.02 mg g^{-1} and 9.63 mg g^{-1}, respectively (Figure 8). Thus, the TC adsorption onto poly(HEMA)-CB is higher than the adsorption onto poly(HEMA). The higher adsorption of TC onto poly(HEMA)-CB can be based on the increased number of binding sites due to covalently attached CB.

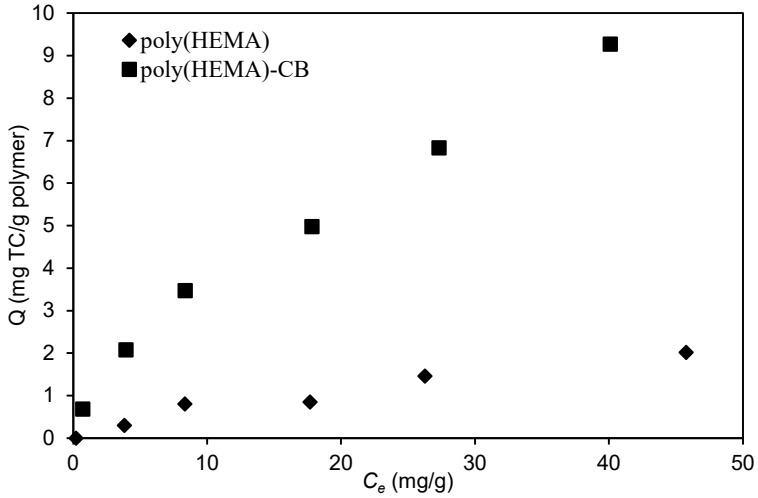


Figure 8. TC adsorption onto poly(HEMA) and poly(HEMA)-CB (C_{TC} = 10 mg/L; T = 25 °C; $m_{poly(HEMA)-CB}$ = 0.02 g; V = 20 mL)

4. Conclusion

Tetracycline is an important endocrine-disrupting chemical (EDC) and can be effectively removed from aquatic solutions or waste waters. Adsorption is an easy, low cost and attractive method for water treatment. The main goal of this study is to prepare an effective adsorbent for TC removal from aqueous solutions. Dye attached poly(HEMA) microbeads have good adsorption capacity for TC and they can be used repeatedly for five times without losing their efficiencies.

In this study, Cibacron Blue G3FA-attached poly(HEMA) microbeads were synthesized, characterized, and used as adsorbent for tetracycline adsorption from aqueous solution. The optimum pH value and temperature for the adsorption of TC were determined to be 7.0 and 25 °C, respectively. All adsorption experiments were performed at this optimum pH value and temperature. The maximum adsorption capacity (Q) of the poly(HEMA)-CB was determined to be 9.63 mg g^{-1} at 25 °C. In addition, decreasing the temperature from 12 °C to 4 °C decreased Q by 5.16 mg g^{-1} to 0.99 mg g^{-1}. Isotherm models such as Langmuir, Freundlich, and D-R models were used to represent the adsorption process. The mean values of the thermodynamic parameters of the standard entropy ($\Delta S°$= 0.29 kJ mol^{-1} K^{-1}), standard enthalpy ($\Delta H°$= 69.26 kJ mol^{-1}) and standard free energy of the adsorption were determined. In conclusion, the CB-attached poly(HEMA) microbeads were used as adsorbents for TC, and the nature of the adsorption process was discussed.

Conflicts of interest

The autors state that they have no conflict of interests.

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