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Polymeric Microspheres for Efficient Adsorption of Reactive Black 5 Dye: Adsorption Isotherms, Kinetics and Thermodynamic Evaluations

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ABSTRACT

In parallel with the increasing human population, industry is growing rapidly, which also causes an increase in the amount of wastewater. Dyes, which represent the largest group of pollutants in wastewater, are utilized in various industries, mainly in the textile sector. In addition to the annual production of tons of dyes, significant quantities of dye-contaminated wastewater are released into the environment. In this study, poly(ethylene glycol dimethacrylate-N-methacryloyl-L-tryptophan methyl ester) (PEDMATP) microspheres were employed to adsorption one of the synthetic dyes, reactive black 5 (RB5), from the aqueous medium. The impacts of parameters such as pH, initial concentration, temperature, and contact time on adsorption were examined. The maximum RB5 adsorbed amount onto PEDMATP was determined as 20.06 mg/g at 277 K and pH=7. The data obtained are compatible with the Langmuir isotherm and pseudo-second-order kinetic models. The polymeric microspheres could be reused up to 5 times with negligible losses (approximetly 15%) of adsorption capacity.

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Keywords: *Adsorption, Dyes, Polymeric microspheres, Reactive black 5*

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1. Introduction

As industry and society grow rapidly at an unprecedented pace, the urgent demand for clean water has never been more critical. Increasing clean water consumption causes the formation of wastewater containing different types of pollutants. Dyes are one of the most significant environmental pollutants and are found in large quantities in wastewater [1,2]. Dyes are natural or synthetic chemical compounds that basically can bind to surfaces and impart color [3]. They are commonly utilized in various sectors, including textiles, leather, paper, printing, rubber, cosmetics, pharmaceuticals, food processing, and plastics [3, 4]. Today, it is known that there are over 100,000 commercial dyes, with annual production quantities over 7 x 10^5 tons [3]. Due to the widespread use of dyes, large amounts of wastewater are produced and released into the environment. Dye pollutants present in the environment pose a significant threat to both humans and aquatic life. Dyes cause coloration in water even when present in small concentrations, and this reduces light transmittance, leading to decreased photosynthesis and adverse effects on aquatic organisms and plants [1]. They can also adversely affect human health, such as carcinogenic, mutagenic, allergic, cardiological, neurological, and reproductive systems [4].

Synthetic dyes produced using various organic molecules are widely used in various industries, especially in the textile industry. These dyes have complex molecular structures, and are typically inexpensive, stable, and hard to biodegrade [1-4]. Reactive black 5 (RB5), one of the synthetic dyes, is widely used in the textile industry to dye nylon, wool, silk, and cotton fabrics due to its vivid color. Due to its widespread use, it can be found in high amounts in most wastewater. Long-term exposure to RB5 has been associated with a variety of adverse health effects. Therefore, the removal of RB5 from aquatic environments is crucial for the protection of human health and the environment [5].

Various methods have been utilized to remove RB5, including coagulation [6], ozonation [7], advanced oxidation [8], membrane separation [9] and adsorption [10]. Adsorption is one of the most widely used due to its inexpensive, rapid treatment, simplicity, availability, various adsorbent types, and effectiveness in eliminating dyes in the environment [2]. Activated carbon [11], zeolite [12], carbon nanotubes [13], polymers [14, 15], chitosan-based materials [16], clay [17], and multi-walled carbon nanotubes [18] have been employed for the removal of RB5. Polymers (nanoparticles and microspheres) are especially attractive because they are materials with superior properties, such as high adsorption capacity, reusability, high pore volume, and pore size. Polymeric

microspheres called poly (ethylene glycol dimethacrylate-N-methacryloyl-L-tryptophan methyl ester) (PEDMATP) synthesized by Osman et al. (2013) were used for the removal of phthalates, bisphenol A, metal, and various pollutants [19-23].

This study focused on RB5 removal from water using PEDMATP polymeric microspheres. The microspheres were synthesized using a procedure developed in our previous study [19]. The effects of parameters such as pH, initial concentration, temperature, and contact time, which are effective on the adsorption process, were investigated. The adsorption behavior was analyzed further through isothermal, kinetic, and thermodynamic studies. The reusability of the microspheres was investigated.

2. Experiment

2.1. Chemicals and Instrumentation

Polyvinyl alcohol, l-tryptophan methyl ester hydrochloride, methacryloyl chloride, and RB5 were obtained from Sigma-Aldrich. Ethylene glycol dimethacrylate, 2,2'-azobisisobutyronitrile, and other chemicals were obtained from Merck. All chemicals are analytical grade. A Mettler Toledo pH meter was used to adjust the pH of the RB5 solutions. Ultrapure water was supplied via the Elga Flex3 water purification system (Veloia Water Solutions & Technologies, France).

2.2. Synthesize and Characterization of PEDMATP Microspheres

PEDMATP polymeric microspheres were successfully synthesized through suspension polymerization as reported by Osman et al. (2013) [19]. In the synthesis procedure, polyvinyl alcohol (0.2 g) and pure water (50 mL) were used in the aqueous phase. The organic phase consisted of a monomer (N-methacryloyl-L-tryptophan methyl ester) (MATP), crosslinker (EGDMA) (5 mL), pore former (toluene) (10 mL), and initiator (AIBN) (0.1 g). The reaction started at 65 °C by distributing the prepared organic phase in the aqueous phase, gradually increasing the temperature. The reaction was carried out for 8-10 hours, and at the end of the period, it was washed with ethanol-water mixture, and polymeric microspheres became ready for use.

The chemical structure of PEDMATP microspheres were studied by FTIR spectrometer (Perkin Elmer, Spectrum 100, USA). The surface morphology of the synthesized microspheres was examined using a scanning electron microscope (Jeol, JEM 1200EX, Tokyo, Japan).

2.3. Adsorption Studies

The influence of pH, initial dye concentration, temperature, and contact time on the adsorption of RB5 was examined to assess the adsorption capacity of the PEDMATP polymeric microspheres. To investigate the effect of pH on the adsorption capacity of the microspheres, various pHs of the RB5 solution between 3.0 and 10.0 were studied. The pHs of the RB5 solutions were adjusted using NaOH (1 M) and HCl (1 M) solutions. The pH effect was examined by suspending 25.0 mg of microspheres in 10 mL of an aqueous solution containing 25 mg/L RB5, which was incubated for 120 minutes at a temperature of 298 K. The effect of initial concentration on adsorption was evaluated by studying different RB5 solution concentrations ranging from 5 mg/L to 100 mg/L. Experiments were carried out with 25.0 mg microspheres in 10 mL of RB5 solution at different temperatures (277 K, 298 K, and 308 K). All experimental studies were conducted with a minimum of three replicates for each trial. The absorbance values of the initial and final RB5 solutions in the adsorption experiments were measured by a Shimadzu UV-1700 spectrophotometer at a wavelength of 597 nm. The adsorbed amount of RB5 was calculated according to Equation (1).

$$qe = \frac{[(C_0 - C)\,V]}{m} \quad (1)$$

where qe is equilibrium adsorption capacity (mg/g); C_0 is the initial, and C is the final RB5 dye concentration after adsorption (mg/L); V is the volume of the dye solution (L); m is the amount of the sorbent used in the experiment (g).

2.4. Reusability Studies

In order to determine the reusability of PEDMATP polymeric microspheres for RB5 adsorption, the adsorption process was carried out sequentially. The experiments were carried out under the optimum experimental conditions of initial concentration of RB5 solution as 25 mg/L, sample volume as 10 mL, sorbent amount as 25 mg, adsorption time as 120 min, and temperature as 277 K. The desorption of RB5 on microspheres was achieved by 0.1 M sodium chloride in ethanol solution.

3. Results and Discussion

3.1. Characterization of PEDMATP Microspheres

FTIR analysis was operated for the chemical characterization of the PEDMATP microspheres. In the FTIR spectrum (Figure 1), an amide carbonyl group (C=O) stretch at 1662 cm^{-1} and an ester carbonyl group (C=O) stretches at 1715 cm^{-1} were obviously observed. The absorption band at 3403 cm^{-1} resulting from the N–H stretching in the structure of the MATP monomer existed. These results showed that the functional monomer MATP was successfully added into the polymeric microspheres.

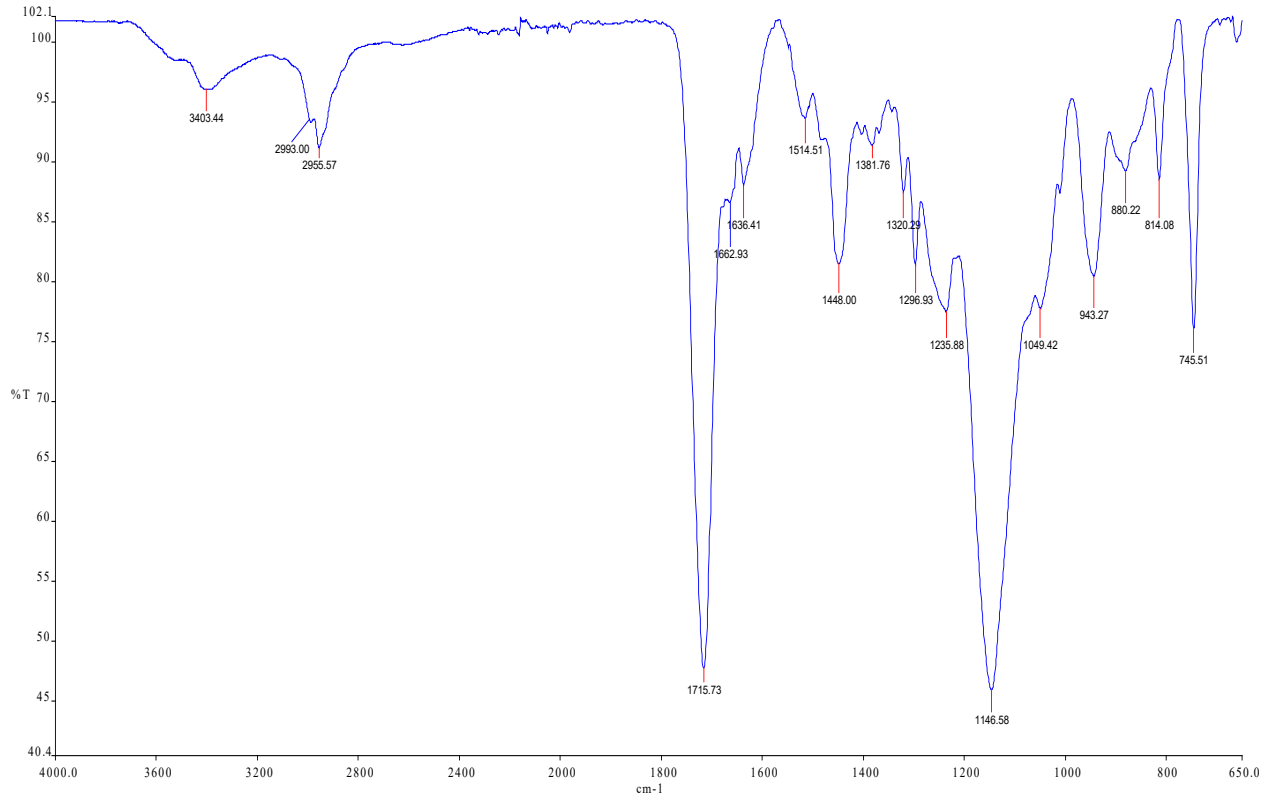

Figure 1. FTIR spectrum of the PEDMATP microbeads.

The morphological properties of the PEDMATP microbeads are evaluated by SEM analysis. Figure 2 demonstrated that the microbeads exhibited a uniform, spherical shape with porous surface structure, which is superior for increasing diffusion and surface interaction with analytes (Figure 2). PEDMATP microspheres were seen to have a regular spherical geometry and almost the same size.

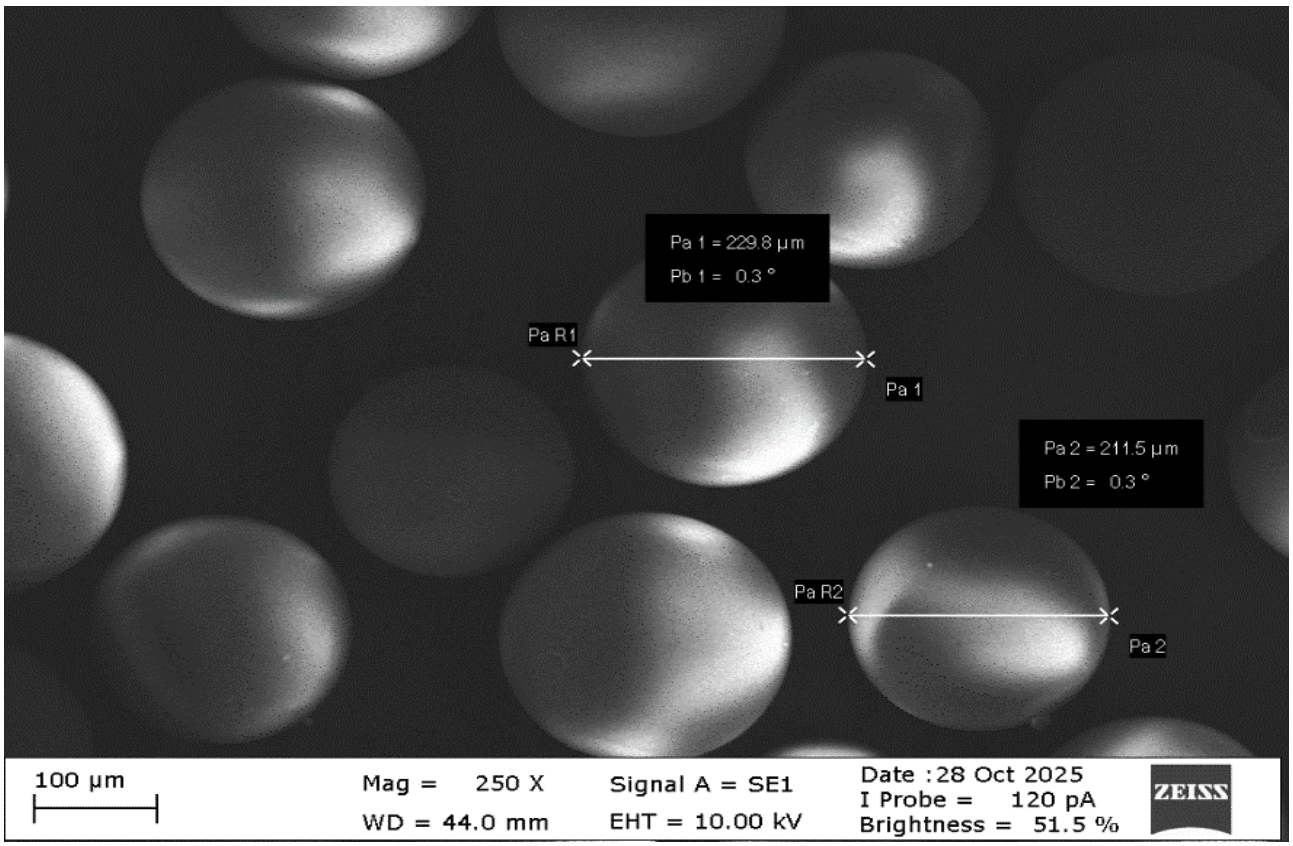

Figure 2. SEM image of the PEDMATP microbeads.

3.2. Effect of pH

One of the most important factors affecting the adsorption mechanism between the sorbent and the analyte is the pH of the aqueous medium. The pH of a solution affects both the surface charge of the adsorbent and the ionization level of the solute [24]. Adsorption experiments were carried out by adjusting the pH values of RB 5 solutions between 3 and 10. The relationship between pH and adsorption capacity was investigated under the experimental conditions of 25 mg/L RB5 dye concentration at 298 K, 25 mg polymer, and 120 min contact time. As seen in Figure 3, the adsorption capacity of RB5 dye solution increased when the pH was increased from 3 to 7, achieving a maximum capacity of 6.540 mg/g at pH 7. At low pH values, hydrogen ions cause a positive charge on the surface of the microspheres. At low pH values, electrostatic repulsions can occur between the sulfonic groups of the RB5 dye and the polymer, decreasing the adsorption capacity. At pH 7, the adsorbent surface is neutral, and hydrogen bonds and Van der Waals interactions can be effective between RB5 and the polymeric microspheres. As the pH increases from 7 to 10, the concentration of -OH ions in the solution increases significantly. This creates a competitive environment between RB5, an anionic dye, and hydroxide ions for the binding sites on the polymeric microspheres. As a result, the adsorption capacity for RB5 decreases due to this competition. The study was continued at pH 7, where maximum adsorption was obtained.

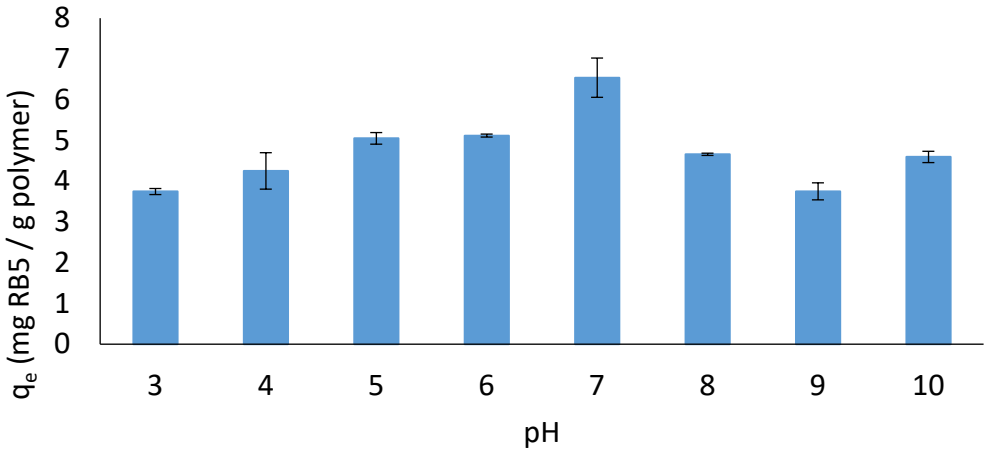

Figure 3. Effect of pH on RB5 adsorption capacity on microspheres.

3.3. Adsorption Isotherms

The effect of initial RB5 concentration on the adsorption capacity of the microspheres was investigated under the experimental conditions of 25 mg/L RB5 dye, 25 mg polymer, and 120 min contact time. In Figure 4, the results demonstrate a significant increase in the amount of adsorbed RB5 as the concentration increased from 5 to 100 mg/L at three different temperatures. The maximum amounts of RB5 dye adsorbed on the microspheres were determined to be 20.06 mg/g at 277 K, 12.83 mg/g at 298 K, and 10,85 mg/g at 308 K. The amount of RB5 adsorbed on the microspheres increased with decreasing temperature, demonstrating that the adsorption process was exothermic.

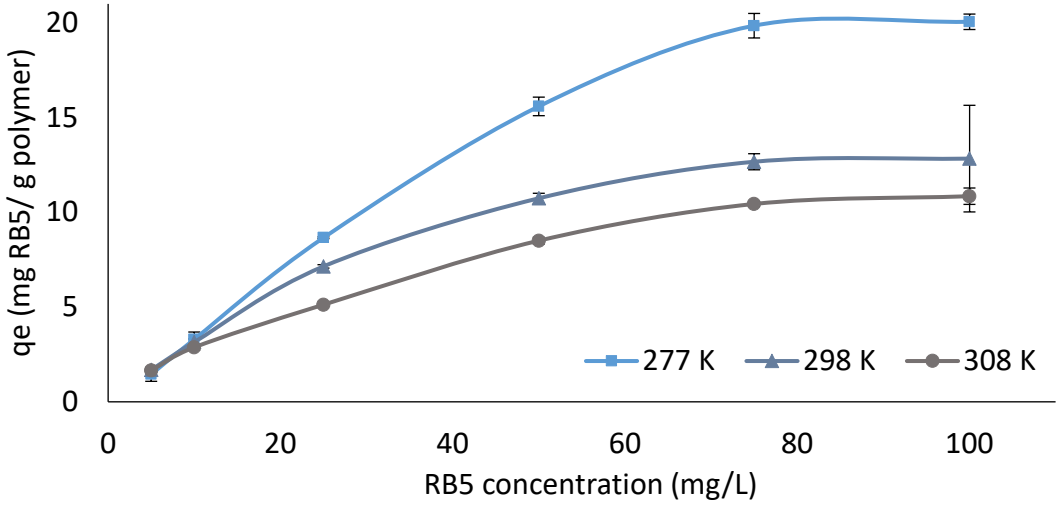

Figure 4. Effect of initial concentration on RB5 adsorption capacity on microspheres.

The experimental data obtained from adsorption of various initial RB5 dye concentrations at different temperatures were analyzed to understand the equilibrium relationship between the dye concentration in the solution and the amount of RB5 adsorbed onto the PEDMATP polymeric microspheres. The experimental adsorption data were fitted to the Langmuir and the Freundlich adsorption isotherm models via MATLAB 2018 Curve Fitting Tool. The Langmuir and Freundlich adsorption isotherm models are commonly utilized to study the characteristics of adsorbent surfaces. The Langmuir model describes monolayer sorption onto a surface with a finite number of identical sites, while the Freundlich model is based on sorption onto a heterogeneous surface [25]. The Langmuir and Freundlich equations are given by Equation (2) and (3), respectively.

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

where Ce is the concentration of RB5 dye at equilibrium (mg/L); qe is the amount of dye adsorbed at equilibrium (mg/g); QL is maximum adsorption capacity at equilibrium (mg/g) for monolayer adsorption, and K_L is the Langmuir equilibrium constant (L/mg) related to the affinity of the binding sites.

In the Freundlich isotherm model, adsorption occurs through multiple layers and the adsorbate concentration on the adsorbent surface increases with increasing adsorbate concentration. The Freundlich equation is given by Equation (3):

$$lnq_e = lnK_f + \frac{1}{n} lnC_e \quad (3)$$

where K_F is the Freundlich equilibrium constant (mg/g)(L/mg)$^{1/n}$, C_e is the concentration of RB5 dye at equilibrium (mg/L), q_e is the amount of dye adsorbed at equilibrium (mg/g) and n (1< n <10) is the Freundlich constant representing the heterogeneous surface.

The isotherm parameters calculated for the isotherm models are given in Table 1. The analysis indicated that the Langmuir isotherm model exhibited higher R^2 adj values (>0.9832) along with lower root mean square error (RMSE) and standard square error (SSE) values. In contrast, the R^2 adj values for the Freundlich isotherm model ranged between 0.9500 and 0.9882, with corresponding RMSE and SSE values exceeding those of the Langmuir model. The best-fitting model is characterized by the lowest RMSE and SSE values, alongside an R^2adj close to 1. Hence, it can be concluded that the Langmuir isotherm model aligns well with the experimental data based on the model parameters.

Table 1. Isotherm model parameters for RB5 adsorption.

Langmuir isotherm model			
Temperature (K)	**277**	**298**	**308**
Q_{exp} (mg/g)	20.06	12.83	10.85
Q_{max} (mg/g)	32.30	14.33	20.44
K_L (L/mg)	0.08196	0.1309	0.02454
R^2	0.9865	0.9902	0.9968
R^2_{adj}	0.9832	0.9878	0.9960
RMSE	1.063	0.5336	0.247
SSE	4.524	1.139	0.2441
Freundlich isotherm model			
Temperature (K)	**277**	**298**	**308**
K_F (mg/g)(L/mg)$^{1/n}$	3.342	3.157	0.827
n	1.661	2.858	1.475
R^2	0.9608	0.9600	0.9906
R^2_{adj}	0.9510	0.9500	0.9882
RMSE	1.814	1.08	0.4263
SSE	13.17	4.665	0.7268

3.4. Adsorption Kinetics

In order to investigate the effect of time on adsorption, it was studied under experimental conditions with a 75 mg/L RB5 dye solution (30 mL) and 75 mg microspheres at different temperatures (277 K, 298 K, and 308 K). The results shown in Figure 5 indicated that RB5 adsorption was rapid during the first 30 minutes. Additionally, the adsorption capacity increased with lower temperatures, suggesting that the adsorption process was exothermic. The RB5 adsorption capacities of microspheres were 20.32 mg/g at 277 K, 15.19 mg/g at 298 K, and 12.69 mg/g at 308 K.

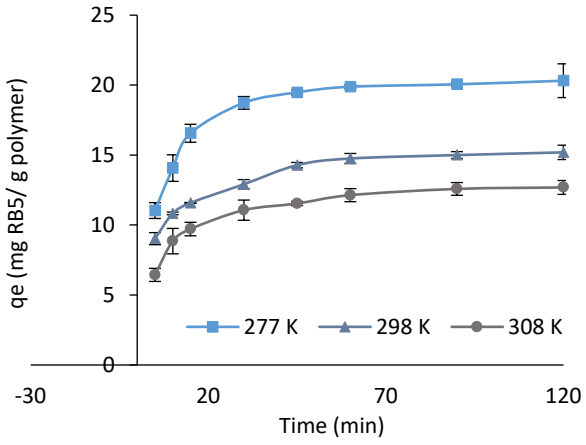

Figure 5. Effect of contact time on RB5 adsorption on microspheres.

Kinetic models are crucial for understanding the equilibrium time between the adsorbent and the solution in the adsorption process. The adsorption kinetics of RB5 on microspheres were evaluated using pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order kinetic model is given by Equation (4) [26]:

$$\frac{d_q}{d_t} = k_1 (q_e - q_t) \quad (4)$$

where q_e (mg/g) and q_t (mg/g) are the amount of RB5 dye adsorbed at equilibrium and at any time t, respectively. t is the contact time (min) and k_1 represent the rate constant pseudo-first-order adsorption (1/min). The equation of the pseudo-first-order kinetic model is given in Equation (5).

$$q_t = q_e [1 - \exp(-k_1 t)] \quad (5)$$

The pseudo second-order kinetic model is given by Equation (6) [27]:

$$q_t = \frac{k_2 {q_e}^2 t}{1 + q_e k_2 t} \quad (6)$$

where k_2 is the pseudo-second-order rate constant at the equilibrium ((g/mg)/min) and q_e and q_t (mg/g) have the same definitions as in Equation (4).

The parameters calculated for both the pseudo-first-order and pseudo-second-order kinetic models are presented in Table 2. Upon examining the adjusted correlation coefficients (R^2adj) obtained from these models, it was found that the pseudo-second-order kinetic model yielded the highest R^2adj values, exceeding 0.9581. Furthermore, the experimental values of Q_{exp} closely matched the calculated values of qe. In contrast, the RMSE and SSE were higher for the pseudo-first-order kinetic model. Overall, the results indicate that the adsorption data aligns well with the pseudo-second-order model.

Table 2. Kinetic model parameters for RB5 adsorption on microspheres.

Pseudo first-order kinetic model			
Temperature (K)	**277**	**298**	**308**
Q_{exp}(mg/g)	20.32	15.19	12.69
q_e (mg/g)	19.69	14.31	12.02
k_1 (1/min)	0.1376	0.1532	0.1317
R^2	0.9577	0.8130	0.9290
R^2_{adj}	0.9507	0.7819	0.9171
RMSE	0.7507	1.059	0.6242
SSE	3.381	6.735	2.338
Pseudo second-order kinetic model			
Q_{exp} (mg/g)	**20.32**	**15.19**	**12.69**
q_e (mg/g)	21.34	15.47	13.14
k_2 (1/min)	9.98×10^{-3}	1.55×10^{-2}	1.47×10^{-2}
R^2	0.9937	0.9641	0.9953
R^2_{adj}	0.9926	0.9581	0.9945
RMSE	0.2902	0.4642	0.1614
SSE	0.5043	1.293	0.1562

The adsorption rate constants at different temperatures are used to calculate the activation energy (Ea, kJ/mol) required for the adsorption of the adsorbate molecule to the adsorbent surface with Equation (7).

$$ln\, k = ln\, k_o - \frac{Ea}{RT} \quad (7)$$

The following parameters are defined: Ea represents the adsorption activation energy (measured in kJ/mol), T is the temperature of the RB5 solution (K), R is the gas constant (8.314 J/mol K), k_0 is the independent temperature factor ((g/mg)/min), and k is the adsorption rate constant ((g/mg)/min). An adsorption process is classified as physical adsorption when the activation energy, Ea, is less than 40 kJ/mol. For the adsorption of RB5, Ea was determined to be 9.84 kJ/mol. Since the calculated activation energy for RB5 adsorption was less than 25 kJ/mol, the adsorption rate on the microspheres is primarily controlled by diffusion [26, 27].

3.5. Thermodynamic Analysis

Adsorption thermodynamics is utilized to describe the performance of adsorption processes. The thermodynamic parameters, including Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°), were calculated in detail for the adsorption of RB5 onto the microspheres. These parameters were determined using Equation (8).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

The relationship of adsorption with ΔG^o and the equilibrium constant Kc is expressed by the Van't Hoff equation (9).

$$lnKc = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) \quad (9)$$

The nonlinear equations of the Langmuir and Freundlich isotherm models were used to calculate the isotherm model parameters and thermodynamic parameters for RB5 adsorption onto the microspheres. In Equation (2), Qmax represents the maximum monolayer adsorption capacity when the adsorbate fully occupies all surface binding sites. The K_L constant is measured in (L/mg), but it is important to note that K_C must be a unitless value. Consequently, using K_L directly in its (L/mg) form can lead to erroneous calculations of thermodynamic parameters, as highlighted by several studies [28]. Fortunately, K_C can be calculated without any units using two distinct methods [29]. The thermodynamic parameters for the adsorption of RB5 onto the microspheres calculated from K_L are detailed in Table 3.

Table 3. Thermodynamic parameters calculated from K_L values.

T(K)		$K_C = K_L$			
	van't Hoff equation	K_C	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (kJ/mol K)
277	y = 900.32x – 5.0935 R^2 = 0.0073	0.082	4.244	-7.480	-0.042
298		1.131	5.134		
308		0.024	5.557		
		$K_C = K_L x 10^6$			
277	y = 900.32x + 8.722 R^2 = 0.0073	81960	-27.571	-7.480	0.072
298		1130900	-29.094		
308		24540	-29.819		
		$K_C = M_W x 55{,}5 x 1000 x K_L$			
277	y = 9993.3x – 19.563 R^2 = 0.2176	4511571	-38.038	-83.080	-0.162
298		62251533	-34.622		
308		24339	-32.996		

The Freundlich isotherm equation, on the other hand, is compatible with the thermodynamics of heterogeneous adsorption. K_F, Freundlich constant, is converted to unitless *Kc* via Equation 11 [30].

$$K_c = \frac{K_F\,\rho}{1000}\left(\frac{10^6}{\rho}\right)^{\left(1-\frac{1}{n}\right)} \quad (11)$$

The notation ρ represents the density of pure water, which is approximately 1 g/mL. Table 4 contains the thermodynamic parameters for the adsorption of RB5 onto the microspheres, as calculated using K_F.

Table 4. Thermodynamic parameters calculated from K_F values.

T(K)		$K_C = K_F$			
	van't Hoff equation	K_C	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (kJ/mol K)
277	y = 3201.4x – 10.176 R^2 = 0.5705	3.342	-3.195	-26.610	-0.084
298		3.157	-1.419		
308		0.827	-0.574		
		$K_C = \frac{K_F\ \rho}{1000}\left(\frac{10^6}{\rho}\right)^{\left(1-\frac{1}{n}\right)}$			
277	y = 8592.02x – 16.802 R^2 = 0.4446	816065	-32.721	-71.430	-0.139
298		1258040	-29.786		
308		16056	-28.388		

Several factors are important in determining thermodynamic parameters. Firstly, the K_C constant must be unitless, which is essential. Additionally, a high R^2 value for the van't Hoff equation, utilized in calculating these parameters, is crucial for accuracy. It's also important to select the isotherm model that provides the best fit to determine the K_C constant. Furthermore, the thermodynamic parameters obtain ed should establish a significant relationship with experimental data. In this context, even though the R^2_{adj} values from the Langmuir isotherm model are high and the RMSE and SSE values are comparatively low when measured against the Freundlich isotherm model, the thermodynamic parameters derived from the Langmuir constant K_L lack validity and do not align with experimental results. Furthermore, the R^2 value of the van't Hoff equation is notably low (0.0073 as shown in Table 3). Therefore, while the adsorption data might be explained using the Langmuir isotherm model, it becomes evident that the K_L constant is not appropriate for the calculation of thermodynamic parameters.

When examining the thermodynamic parameters calculated using the K_F constant derived from the Freundlich isotherm equations, it was observed that the R^2 value of the van't Hoff equation was high (Table 4). In addition, it was observed that the obtained ΔG° (kJ/mol) and ΔH° (kJ/mol) values were compatible with the spontaneous and exothermic nature of the adsorption process. The ΔG° (kJ/mol) values derived directly from the K_F constant from the Freundlich equation in the calculation of thermodynamic parameters were -3.195, -1.419, and -0.574 kJ/mol for 277 K, 298 K, and 308 K, respectively (Table 5). The ΔG° (kJ/mol) values calculated by converting the K_F constant into the unitless K_C equilibrium constant were -32.721, -29.786, and -28.388 kJ/mol for 281 K, 298 K, and 308 K, respectively. The ΔH° and ΔS° values were determined to be -71.430 kJ/mol and -0.139 kJ/mol K, respectively. As a result, RB5 adsorption onto the microspheres is favorable and spontaneous.

3.6. Reusability Studies

To demonstrate the reusability of the PEDMATP polymeric microspheres, the adsorption/desorption cycles were repeated five times using the same microspheres. After five consecutive adsorption/desorption cycles, the RB5 adsorption capacity of the microspheres did not significantly change. The amounts of adsorbed RB5 varied between 7.27 and 6.19 mg/g (Figure 6). The microspheres maintain their ability to adsorb at a ratio of 85.14% and it can be reused without a significant decrease in adsorption capacity.

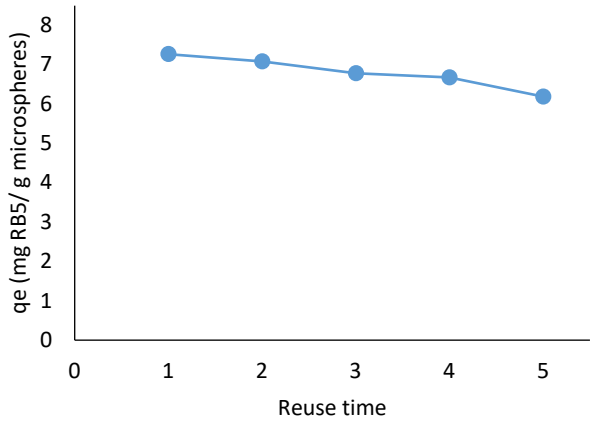

Figure 6. Reusability of microspheres.

Table 5 summarizes the adsorption capacities of various adsorbents reported in the literature and compares them with the PEDMATP polymeric microspheres. The adsorption capacity of the previously reported adsorbents (carbon nanotubes, nanoparticles, clay, chitosan-based materials, activated carbon, etc.) for RB5 adsorption ranges from 0.606 to 833.3 mg/g. The PEDMATP microspheres have a moderate adsorption capacity.

Table 5. Comparison of RB5 adsorption capacities of the various adsorbent reported in literature.

Adsorbent	Analytes	Matrices	Experimental conditions		Adsorption capacity (qe)	References
Carbon Nanotubes	RB5	Aqueous solution	100 mg adsorbent 298 K	pH=3 60 min	829.20 mg/g	[13]
Titanium dioxide nanoparticles	RB5	Aqueous solution	175 mg adsorbent 303 K	pH= 6 60 min	88.495 mg/g	[14]
Quaternized 2-dimethylaminoethyl methacrylate based polymer/clay nanocomposites	RB5	Aqueous solution	50 mg adsorbent 313 K	pH=11.3 500 min	833.3 mg/g	[15]
Bentonite Clay	RB5	Aqueous solution	50 mg adsorbent 323 K	pH=10 60 min	34.01 mg/g	[17]
Chitosan-Deep Eutectic Solvent Beads	RB5	Wastewater	15 mg adsorbent 318 K	pH=6 240 min	379.90 mg/g	[31]
Chitosan	RB5	Aqueous solution	50 mg adsorbent 323 K	pH=4 120 min	62.92 mg/g	[32]
Macadamia seed husks	RB5	Aqueous solution	2500 mg adsorbent 298 K	pH=3 600 min	1.1436 mg/g	[33]
Powdered activated carbon (PAC) and fly ash (FA)	RB5	Aqueous solution	100 mg adsorbent 293 K	pH= Natural dye pH 60 min	PAC: 58.823 mg/g FA: 7.936 mg/g	[34]
Chemically modified banana peel powder	RB5	Aqueous solution	50 mg adsorbent 298 K	pH=3 180 min	211.8 mg/g	[35]
Silica–polyacrylamide composite particles	RB5	Aqueous solution	10 mg adsorbent 298 K	pH=2 60 min	454.54 mg/g	[36]
Powdered activated carbon coated with zinc oxide nanoparticles	RB5 Reactive Blue 19	Aqueous solution	1.5 g/L adsorbent 298 K	pH=3 30 min	RB5: 71.42 mg/g RB19: 94.33 mg/g	[37]
Active carbon sorbent immobilized-cationic surfactant	RB5	Real textile wastewater, tap water, and sea water	20 mg adsorbent 313 K	pH=2 10 min	77.52 mg/g	[38]
Eichhornia crassipes/chitosan composite	RB5	Aqueous solution	1000 mg adsorbent 298 K	pH=3 30 min	0.606 mg/g	[39]
Multi -walled carbon nanotubes	RB5	Aqueous solution	500 mg adsorbent 90 min	- pH=7	36.2 mg/g	[40]
Poly (ethylene glycol dimethacrylate-N-methacryloyl-L-tryptophan methyl ester) (PEDMATP) microspheres	RB5	Aqueous solution	25 mg adsorbent 277 K	pH=7 120 min	20.06 mg/g	In this study

4. Conclusion

Poly (ethylene glycol dimethacrylate-N-methacryloyl-L-tryptophan methyl ester) (PEDMATP) polymeric microspheres were employed for the removal of RB5 from aqueous media. The effects of parameters such as pH (3-10), initial dye concentration (5-100 mg/L), temperature (277, 298, and 308 K), and contact time (5-120 min) on adsorption were investigated. Optimum adsorption parameters were determined at pH=7, 120 min, and 277 K using 25 mg of sorbent. Adsorption studies were conducted under optimum conditions, and the obtained data were applied to various isotherm and kinetic models. It was found that the adsorption process was exothermic. According to the obtained data, it was observed that it was compatible with the Langmuir model among the isotherm models and with the pseudo-second-order kinetic model among the kinetic models. By evaluating the reusability of polymeric microspheres, adsorption can be conducted 5 times without any significant decrease in adsorption capacity (14.86% loss). This developed method shows substantial potential for removing RB5 from aqueous media using polymeric microspheres.

Conflicts of interest

There are no conflicts of interest in this work.

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