Celal Bayar University Journal of Science

Adsorptive Removal of Tartrazine Dye by Poly(N-vinylimidazole-ethylene glycol dimethacrylate) And Poly(2-hydroxyethyl methacrylate-ethylene glycol dimethacrylate) Polymers

Ayşe Dinçer[1]*, Tülin Aydemir[1]

[1] 1Manisa Celal Bayar University, Faculty of Science and Arts, Chemistry Department,45140, Manisa, Turkey[2]
*ayse.dincer@cbu.edu.tr
*Orcid: 0000-0001-6158-1775

Received: 28 January 2021
Accepted: 29 November 2021
DOI: 10.18466/cbayarfbe. 869963

Abstract

Poly(N-vinylimidazole-ethylene glycol dimethacrylate (P(VI-EGDMA)) and poly(2-hydroxyethyl methacrylate-ethylene glycol dimethacrylate (P(HEMA-EGDMA)) were synthesized as adsorbents for adsorptive removal of tartrazine dye from aqueous solutions. To achieve maximum tartrazine adsorption, some parameters were examined, and pH was found to be an important factor for the adsorption on P(VI-EGDMA). As the temperature increased, removal amount of tartrazine was increased. The experimental capacities were found as 265.5 mg/g and 45.15 mg/g for P(VI-EGDMA) and P(HEMA-EGDMA), respectively. The experimental data well correlated with Freundlich isotherm. The estimated ΔH^o values were found as 12.76 kJ/mol and 10.40 kJ/mol for P(VI-EGDMA) and P(HEMA-EGDMA), respectively. Adsorption was demonstrated to be endothermic in nature. The characterization of these polymers was done by using FTIR, TGA and SEM analysis.

Keywords: Adsorption isotherms, dye removal, poly(N-vinylimidazole-ethylene glycol dimethacrylate), poly(2-hydroxyethyl methacrylate-ethylene glycol dimethacrylate), tartrazine.

1. Introduction

The industry, which develops to encounter the needs of the contemporary world, unfortunately causes environmental pollution. Pollution adversely affects the health of all living organisms and this has many sources. Dyes in industrial wastewaters are one of the pollution sources and they are utilized in many industries such as textile, food, leather, plastics, cosmetics, and paper [1–3] Some dyes can have toxic effects, they can be mutagenic or cancerogenic. Researchers apply different techniques such as electrochemical methods, precipitation, filtration, photocatalytic degradation and adsorption to remove pollutants from wastewaters [4–8]. Among the various techniques, adsorption is measured as most efficient and adaptable in practice. Different researchers have investigated the adsorption of dyes on natural or synthetic materials [9,10].

Tartrazine (E102 or FD&C Yellow 5) is an azobenzene synthetic azo dye and its structure traits a trisodium salt of 3-carboxy-5-hydroxy-1 (p-sulfophenyl)-4-(sulfophenyl azo) pirazolone. This dye is used in many commercial food goods like drinks, soups, pudings, cakes, soups and candies or in medicinal capsules, syrups [11]. It is an alternative colorant to beta carotene to achieve similar color because of its lower price. Excessive consumption of tartrazine can cause allergic reactions, migraines, lupus, hyperactivity and behavioral problems [12,13].

In the present work, adsorption of tartrazine on P(VI-EGDMA), and P(HEMA-EGDMA) polymers using various variables are reported. Adsorption isotherms are applied to understand the mechanisms of dye adsorption onto polymers. The thermodynamic parameters also were evaluated. The characterizations of the adsorbents were done by FTIR, TGA and SEM analysis.

2. Materials and Methods

2.1. Materials

Tartrazine (FD & C Yellow No. 5, C.I. 19140) was provided by KRK Gıda, Istanbul, Turkey. Ethanol, methanol, acetone, 1,1'-azobis(cyclohexane-carbonitrile) (ABCN), acetone, 2-hydroxyethyl methacrylate (HEMA), N-vinylimidazole (VI), acetonitrile (ACN), ethylene glycol dimethacrylate (EGDMA), NaOH and HCl were supplied from Sigma Aldrich (USA).

2.2. Preparation of P(VI-EGDMA), and P(HEMA-EGDMA)

Two types of polymers, based on VI and HEMA as monomers, were prepared. 1 mmol monomer was firstly dissolved in 2 mL ACN (as a solvent) and then 5 mmol EGDMA (as a crosslinker) and 10 mg ABCN (as an initiator) were added to the solution. Then nitrogen gas purged for 5 min to remove the dissolved oxygen. Polymerization was completed after the tubes were incubated at 60°C for 24 h. The consisting polymers were crushed and powdered. Then the polymers were washed by ethanol and acetone to remove the excess of unreacted monomers and dried in vacuo for 24 h.

2.3. Spectrophotometric analysis

The standard tartrazine solutions prepared in distilled water and spectrophotometric measurements were taken at 426 nm where the maximum absorption is observed.

2.4. Characterization

P(VI-EGDMA) and P(HEMA-EGDMA) polymers were characterized by Fourier Transform Infrared (FTIR) Spectroscopy (Spectrum BX, Perkin Elmer), scanning electron microscope (SEM) (Quanta 250 FEG/FEI) and by TGA/DSC (TGA analyzer, Perkin Elmer SII Exstar 7300).

2.5. Adsorption Studies

Batch adsorption experiments were set and the effect of contact time (15-90 min), amount of adsorbent (5-25 mg), pH (pH 2.0-10.0), temperature (20-60°C) and dye concentration (16-1870 mg/L) on tartrazine adsorption was examined. The polymers were removed by centrifugation at the end of the pre-determined times and the unadsorbed tartrazine in the supernatant were analyzed spectrophotometrically.

The following equation (2.1) is used for the calculation of the amount of dye adsorbed on the polymers:

$$\mathrm{qe} = \frac{(\mathrm{Co}-\mathrm{Ce})\,\mathrm{x}\,\mathrm{V}}{\mathrm{m}} \qquad \textbf{(2.1)}$$

qe: the amount of dye adsorbed (mg/g),
Co: the initial dye concentration (mg/L),
Ce: the equilibrium dye concentration (mg/L),
V : the volume of solutions (L)
m: amount of the adsorbent (g).

2.6. Desorption and Reusability studies

The regeneration of the dye adsorbed P(HEMA-EGDMA) was done using 0.01 M NaOH, methanol and acetone, respectively. For the regeneration of the dye adsorbed P(VI-EGDMA), 1 M NaOH, methanol and acetone is used, respectively. Then the polymers were dried and used for the adsorption of the dye again. The equation 2.2 is used to calculate the percentage of tartrazine dye desorbed:

$$\mathrm{D} = \frac{\text{Amount of dye desorbed}}{\text{Amount of dye absorbed}}\ \mathrm{x}\ 100 \qquad \textbf{(2.2)}$$

where D, is the percentage of desorption.

3. Results and Discussion

3.1. Characterization

3.1.1. FTIR Analysis

FTIR spectra of P(VI-EGDMA), and P(HEMA-EGDMA) are given in Fig. 1. The polymers were formerly dried at 60 ºC for 24 h to prevent water-related interferences. For P(VI-EGDMA), the sharp peak at 1732 cm^{-1} is attributed to the stretching of the carbonyl groups of EGDMA. The peaks around 1456 cm^{-1} and 1267 cm^{-1} could be assayed as imidazole group and the peak at 1156 cm^{-1} is stretching vibrations of CH. The peak at 2987 cm^{-1} could be due to CH stretching vibration and the stretching band of OH peak is seen at 3656 cm^{-1}. For P(HEMA-EGDMA), OH stretching vibration spectrum is seen around at 3617 cm^{-1}, CH stretching vibration is seen at 2957 cm^{-1}, carbonyl stretching vibration is at 1731 cm^{-1}, C=C stretching vibrations are at 1455 and 1265 cm^{-1}, and CH stretching vibrations are seen at 1164 and 960 cm^{-1}.

3.1.2. SEM Analysis

SEM analysis gives information about the morphology of the synthesized polymers [14]. As seen from figure 1(b), P(VI-EGDMA) has a porous surface and there are holes and cavities. It should be also noticed that the adsorption capacity was highly depended on the polymer’s surface structure. The porous surface struc ture should be considered as the factor enhancing the surface area. The surface of poly(HEMA- EGDMA) had no surface cavities and this situation negatively affected its dye adsorption capacity.

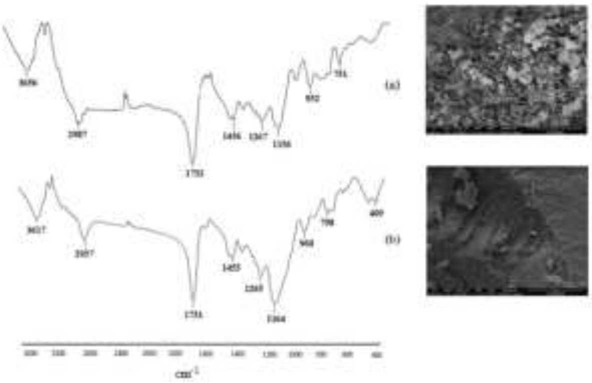

Figure 1. FTIR spectrum and SEM micrographs of (a) P(VI-EGDMA), (b)P(HEMA-EGDMA) (Magnifications: 25.000 ×).

3.1.3. Termogravimetric Analysis

TGA was implemented to determine the chemical composition of the adsorbents. First order derivative of TGA curves reveals the temperature at which the maximum decrease of mass occur [15]. Fig. 2 displays the TGA results of P(VI-EGDMA) and P(HEMA-EGDMA). From the thermal analysis, it was observed that in case of all polymers, the loss of water was observed at the first decomposition stage (30 °C-100 °C). Main mass loss was occurred about 300–500 °C for all polymers. In the first stage of degradation of P(VI-EGDMA) at 310 °C, a mass loss of 21.6 wt.% was observed. On the other hand, degradation of P(VI-EGDMA) took place primarily in the second step of degradation at 425 °C with a very high persistent mass loss of 77.85 wt.%. In the differential thermal gravimetry (DTG) curve of P(HEMA-EGDMA), two peaks were seen at temperatures of 335 °C and 440 °C which show that the weight loss by thermal decomposition occurred in two steps. The weight losses corresponding to these temperature steps were calculated as 45.8 wt % and 82.16 wt %, respectively.

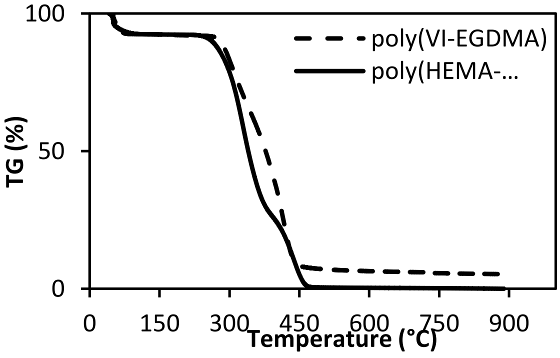

Figure 2. TGA curves of P(VI-EGDMA) and P(HEMA-EGDMA).

3.2. Batch adsorption studies

The contact time is the one of the significant parameters that examined at adsorption studies. Ten milligrams of polymers were added to 16 mg/L tartrazine solution. The contact time was changed from 15 to 90 min then the suspension was centrifuged, and the absorbance of the supernatant was measured. The adsorption efficiency of tartrazine increased in 1 h and the time needed to reach the equilibrium was found as 45 min for these polymers (Figure 3A).

The adsorption studies were performed at 20-60°C to examine the effect of temperature. The adsorption increased with the increasing of the temperature and the maximum adsorption was occurred at 40°C for both polymers (Fig. 3B). The adsorption capacity of the polymers increased with the temperature increase so the solubility of the dye molecules might increase and this may cause the increase in diffusion rate with the expansion of the polymer pores [16].

pH of the dye solution was adjusted to pH 2.0-10.0 by using 0.1 M NaOH or 0.1 M HCl in order to examine the pH effect. Then each polymer was treated with pH adjusted 16 mg/L dye solution. The contact time and the temperature were kept at the optimum values. In this study, dye adsorption was highly dependent to pH of the solution for P(VI-EGDMA). The dye adsorption capacity of P(VI-EGDMA) decreased sharply as the pH levels increased from 2.0 to 8.0. For this polymer calculated adsorption capacity in acidic region was higher than those in other pH values. So, the further assays were done at pH 2.0. At pH 2.0, since the imidazole groups in P(VI-EGDMA) are positively charged and the sulfonic acid groups in the dye are negatively charged, the dye adsorption is at maximum level due to the electrostatic attraction between them. As the pH value increases, especially the charge state of the imidazole groups changes, this time there is a decrease in adsorption because of the repulsion between the polymer and dye molecules. Additionally, at high pH values, there is a competition between OH^- ions and the dye ions causing a decrease in sorption of the dye [17]. P(HEMA-EGDMA) polymer does not contain ionizable groups. However, the OH groups in both HEMA and tartrazine have the capacity to make hydrogen bonds. An interaction occurs between the dye and the polymer through the formation of hydrogen bonds.

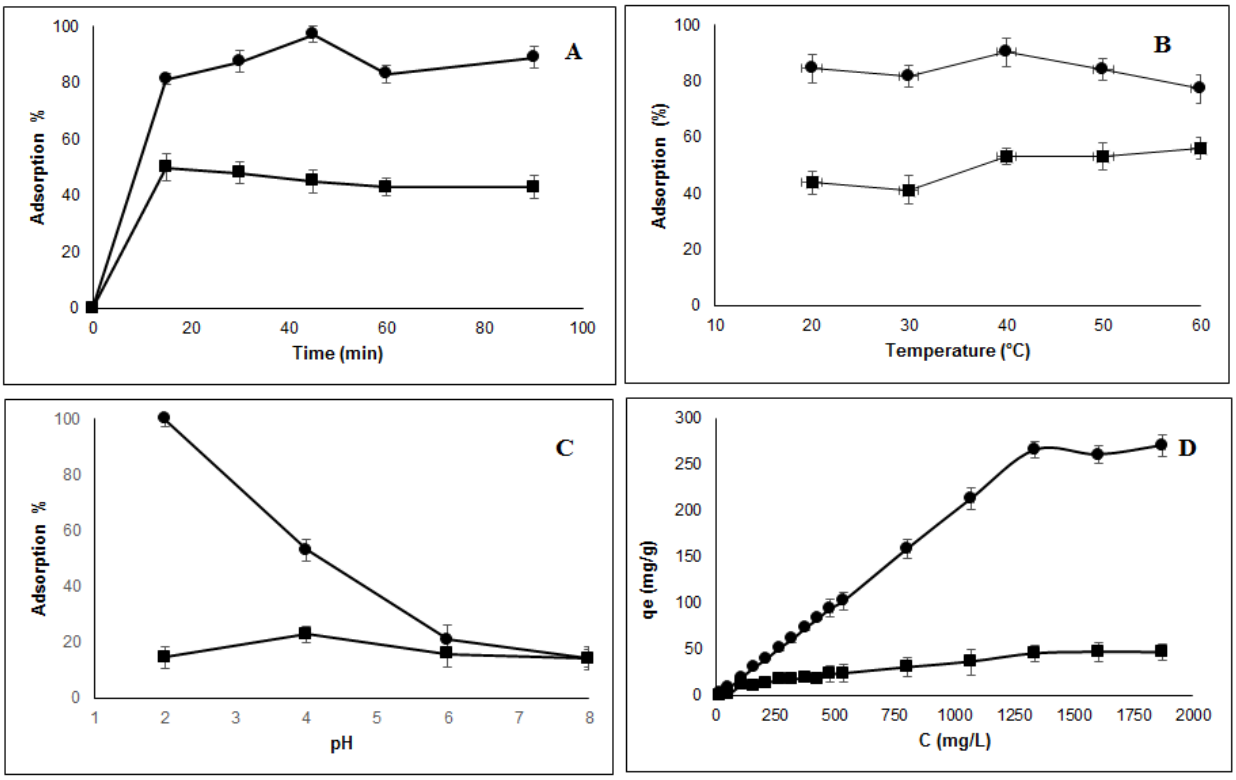

Figure 3.A. Effect of contact time (Tartrazine solution: 16 mg/L, polymer dose 10 mg for P(VI-EGDMA) and 15 mg for P(HEMA-EGDMA). **B.** Effect of temperature (Tartrazine solution: 16 mg/L, incubation time 45 min; polymer dose 10 mg for P(VI-EGDMA) and 15 mg for P(HEMA-EGDMA). **C.** Effect of pH (Tartrazine solution: 16 mg/L, incubation time 45 min, polymer dose 10 mg for P(VI-EGDMA) and 15 mg for P(HEMA-EGDMA), temperature 40 °C.); **D.** Effect of tartrazine concentration (incubation time 45 min; polymer dose 10 mg for P(VI-EGDMA) (-●-) and and 15 mg for P(HEMA-EGDMA) (-■-), temperature 40 °C.).

P(HEMA-EGDMA) is a non-ionic polymer and the sorption of tartrazine on P(HEMA-EGDMA) was found to be pH independent. Also, adsorption of the dye on P(HEMA-EGDMA) were seemed to be negatively affected due to presence of other ions when the pH of the medium was set to a known value by HCl, or NaOH. So, further studies were carried out in aqueous medium for P(HEMA-EGDMA) (Fig 3C).

Effect of dye concentration was studied between 16 mg/L-1870 mg/L tartrazine solution and other parameters were kept at optimum values. As the initial tartrazine concentration increased, the amount of dye adsorbed on P(VI-EGDMA) increased. Dye adsorption on P(HEMA-EGDMA) was not so high as P(VI-EGDMA) and this is due to non-ionic character of the polymer. As shown in Fig. 3D, the amount of dye adsorbed became constant at high dye concentrations. This could be because of saturation of the limited active sites of the adsorbents above a certain dye concentration [18]. Maximum tartrazine adsorption capacities were found as 265.5 mg/g and 45.15 mg/g for P(VI-EGDMA) and P(HEMA-EGDMA) , respectively.

3.3. Thermodynamic parameters

The thermodynamic parameters (ΔG°, ΔH°, ΔS°) are calculated. The following equations (3.1) and (3.2) were used to calculate these parameters, respectively.

$$Kc = Xe / (Ci - Xe) \qquad \textbf{(3.1)}$$

Kc: Equilibrium constant of the adsorption process
Xe: The equilibrium concentration of dye adsorbed, mmol/L,
Ci: The initial dye concentration, mmol/L.

Kc was evaluated at 293, 313, 323 K, and calculated according to Eq. (3) (Table 1). The following equation was used to calculate the free energy (ΔG°):

$$\Delta G° = -RT \ln Kc \qquad \textbf{(3.2)}$$

The standard enthalpy *(ΔH°)* and entropy *(ΔS°)* of the adsorption were determined from the graphic drawn between In Kc vs. 1/T (Fig 4) (Eq 3.3) [19].

$$In\ Kc = (\Delta S°/R) - (\Delta H/RT) \qquad \textbf{(3.3)}$$

R: The gas constant, 8.314 J/mol K
T: The absolute temperature,

ΔH° and ΔS° values were found from the slope. ΔH°/R and the intercept ΔS°/R respectively. The calculated values of the thermodynamic parameters (ΔG°, ΔH°, ΔS°) are shown in Table 2. These results displayed that the adsorption of tartrazine on P(VI-EGDMA) and P(HEMA-EGDMA) is endothermic.

It is obvious that the entropy increases follows: P(VI-EGDMA)>P(HEMA-EGDMA). It means that the adsorbent of P(VI-EGDMA) gave a less order system than P(HEMA-EGDMA) . The negative ΔS° value reflected that no noteworthy changes occurred in the internal structure of P(HEMA-EGDMA) during adsorption of tartrazine. Gibbs free energy change (ΔG°) values were positive and this indicated that adsorption process was unspontaneous.

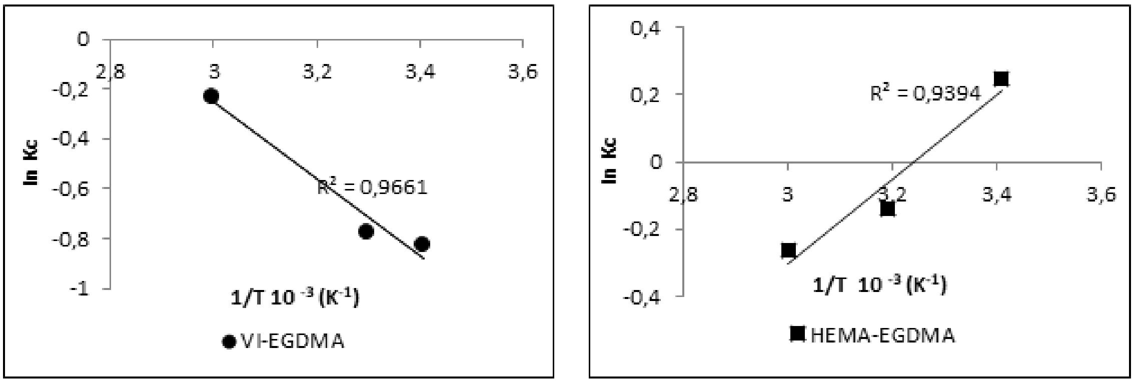

Fig.4. In Kc versus 1/T 10^{-3} for dye adsorption on polymers.

Table 1. Thermodynamic parameters.

Polymer	K*c*			Δ*G*°(kj/mol)			Δ*H*°(kj/mol)	Δ*S*°(J/molK)
	293 K	313 K	323 K	293 K	313 K	323 K		
P(VI-EGDMA)	0.44	0.32	0.43	2.0	2.96	2.22	12.76	36.20
P(HEMA-EGDMA)	1.28	0.87	0.59	-0.60	0.36	1.42	10.40	-33.68

3.4. Adsorption isotherms

The adsorption data was evaluated by linear forms of Freundlich (Eq 3.4) and Langmuir (Eq 3.5) isotherms [20,21].

$$\log qe = \log k_F + 1/n \log Ce \qquad \textbf{(3.4)}$$

qe: amount of dye adsorbed at equilibrium
K_F: adsorption capacity
n: adsorption intensity

When log *qe* was plotted against log *Ce,* 1/*n* value is calculated from the slope. (Fig. 5, Table 3).

$$\frac{Ce}{qe} = \frac{1}{Q_{max}.b} + \frac{Ce}{Q_{max}} \qquad \textbf{(3.5)}$$

Q_{max} : Maximum adsorption capacity (mg/g),
b: (L/mg) Langmuir isotherm constant, relates to adsorption energy (Figure 5). Calculated Langmuir constants Q_{max} and b are displayed in Table 3. Qmax values were found as 102.04 (mg/g) and 76.92 (mg/g) for P(VI-EGDMA) and for P(HEMA-EGDMA) , respectively.

The essential characteristic of the Langmuir isotherm can be defined in terms of a dimensionless equilibrium parameter, R_L, which is usually expressed as (Eq 3.6):

$$R_L = 1/(1+bCo) \qquad \textbf{(3.6)}$$

Where *b* is the Langmuir constant and C_O is the initial dye concentration (mg L^{-1}). The R_L is a measure of whether the adsorption process is favorable or unfavorable.

The isotherms shapes are:

$0 < R_L < 1$	Favorable
$R_L = 1$	Linear
$R_L > 1$	Unfavorable
$R_L = 0$	Irreversible

R_L values were between 0–1, showing that the adsorption process were favorable for P(VI-EGDMA) and P(HEMA-EGDMA) (Table 2). R^2 values of Freundlich isotherms were higher than Langmuir isotherms and displayed the suitability of Freundlich isotherm than Langmuir isotherm. Tartrazine adsorption studies also performed with some adsorbents and adsorption capacities are listed in Table 3.

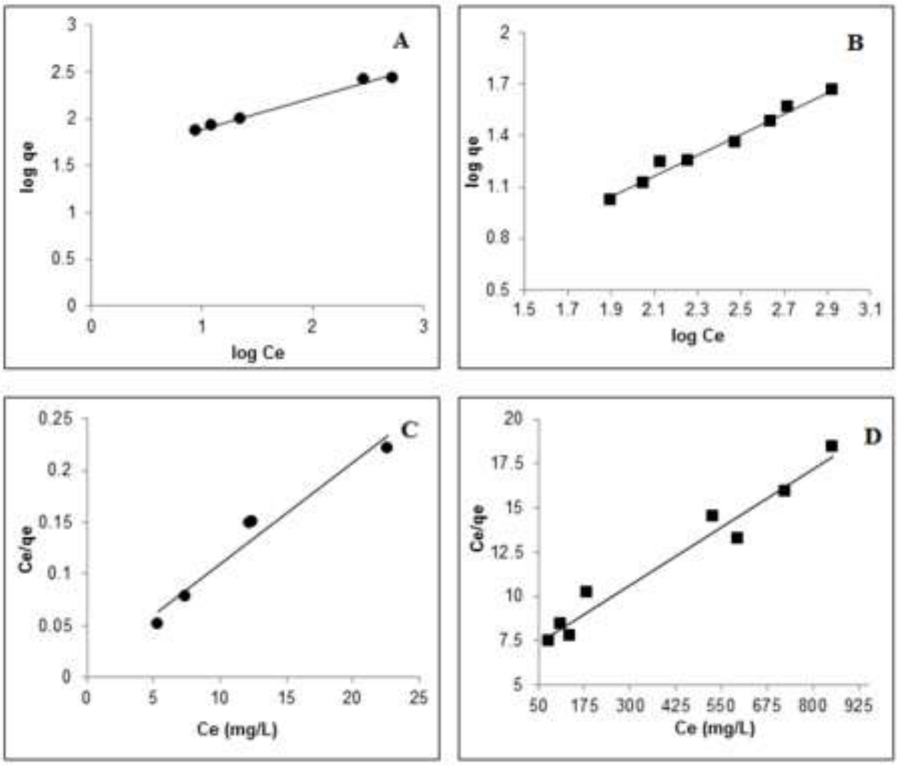

Figure 5: Freundlich (A-B) and Langmuir (C-D) isotherms for tartrazine adsorption on P(VI-EGDMA) (-●-) and P(HEMA-EGDMA) (-■-).

Table 2. Freundlich and Langmuir isotherm parameters

	Freundlich Isotherm			Langmuir Isotherm			
	1/n	K_F	R^2	Q_{max} (mg/g)	b (L/mg)	R_L	R^2
P(VI-EGDMA)	0.34	35.42	0.991	102.04	0.8379	0.001	0.948
P(HEMA-EGDMA)	0.61	1.28	0.982	76.92	0.0019	0.3567	0.961

3.5. Desorption studies and reusability of the adsorbent

The regeneration and reuse of an adsorbent are important from an economic point of view. This study performed at room temperature for all polymers. Adsorption of tartrazine was performed at pH 2.0 on P(VI-EGDMA). Desorption studies were carried out using 1 M NaOH and more than 70% tartrazine could be recovered from the polymer. For the reusability of P(VI-EGDMA), adsorption/desorption cycle was repeated seventeen times. After seventeen usages of the same polymer, the dye binding capacity of P(VI-EGDMA) decreased about 34%. Regeneration of P(HEMA-EGDMA) was done by using 0.01 M NaOH solution. For P(HEMA-EGDMA) recovery of the dye was achieved as about 85%. The reusability of P(HEMA-EGDMA) was successfully performed for five times without significant reduction in adsorption of tartrazine.

Table 3. Comparison of tartrazine adsorption capacities of various adsorbents

Adsorbent type	**Adsorption capacity (mg/g)**	**References**
Activated Red Mud	136.98	[22]
Alkali Activated Fly Ash	174.40	[23]
Lantana carbon	90.9	[24]
Sawdust	4.71	[25]
Silver nanoparticle decorated multiwalled carbon nanotubes	84.04	[26]
In this study		
P(VI-EGDMA)	102.04	
P(HEMA-EGDMA)	76.92	

4. Conclusion

In this study, P(VI-EGDMA), and P(HEMA-EGDMA) were synthesized as adsorbents for removal of tartrazine dye. Optimization of the contact time is necessary to determine the time to reach the equilibrium and for this study it calculated as 45 min for all polymers. The adsorption was highly depended on pH for P(VI-EGDMA) and at pH 2.0 maximum adsorption was obtained. Adsorption on P(HEMA-EGDMA) were not affected by pH and the experiments were performed in aqueous media. The thermodynamic parameters of the adsorption help in prediction of how the adsorption of dye molecules might change with temperature. $\Delta H°>0$ showed that tartrazine dye adsorption on P(VI-EGDMA) and P(HEMA-EGDMA) was endothermic. The adsorption isotherms of P(VI-EGDMA), P(HEMA-EGDMA) were correlated with Freundlich isotherm model.

Author's Contributions

Ayşe DİNÇER, Tülin AYDEMİR: Drafted and wrote the manuscript, performed the experiment and result analysis.
Ayşe DİNÇER, Tülin AYDEMİR: Assisted in analytical analysis on the structure, supervised the experiment's progress, result interpretation and helped in manuscript preparation.

Ethics

There are no ethical issues after the publication of this manuscript.

References

1. El-Sayed, BA, Mohamed, WAA, Galal, HR, Abd El-Bary, HM, Ahmed, MAM.2019. Photocatalytic study of some synthesized MWCNTs/TiO2 nanocomposites used in the treatment of industrial hazard materials. *Egypt Journal of Petroleum*; 28:247–52.

2. Singh, PK, Singh, RL. 2017. Bio-removal of Azo Dyes: A Review. *International Journal of Applied Sciences and Biotechnology*; 5:108–26.

3. Saxena, M, Sharma, N, Saxena, R. 2020. Highly efficient and rapid removal of a toxic dye: Adsorption kinetics, isotherm, and mechanism studies on functionalized multiwalled carbon nanotubes. *Surfaces and Interfaces*; 21:100639.

4. Fatima, B, Siddiqui, SI, Ahmed, R, Chaudhry, SA.2019. Green synthesis of f-$CdWO_4$ for photocatalytic degradation and adsorptive removal of Bismarck Brown R dye from water. *Water Resources and Industry*; 22:100119.

5. Liu, H, Zhang, J, Lu, M, Liang, L, Zhang, H, Wei J. 2020. Biosynthesis based membrane filtration coupled with iron nanoparticles reduction process in removal of dyes. *Chemical Engineering Journal*; 387:124202.

6. Hisada, M, Tomizawa, Y, Kawase, Y.2019. Removal kinetics of cationic azo-dye from aqueous solution by poly-γ-glutamic acid biosorbent: Contributions of adsorption and complexation/precipitation to Basic Orange 2 removal. *Journal of Environmental Chemical Engineering*; 7:103157.

7. Hussain, S, Kamran, M, Khan, SA, Shaheen, K, Shah, Z, Suo, H, Khan, Q, Shah BA, Rehman WU, Al-Ghamdi, YO, Ghadi, U, 2021. Adsorption, kinetics and thermodynamics studies of methyl orange dye sequestration through chitosan composites films. *International Journal of Biological Macromolecules*; 168:383–94.

8. Kong, Q, Wang, X, Lou, T. 2020. Preparation of millimeter-sized chitosan/carboxymethyl cellulose hollow capsule and its dye adsorption properties. *Carbohydrate Polymers*; 244:116481.

9. Morais da Silva, PM, Camparotto, NG, Figueiredo, Neves, T de, Grego, Lira, KT, Mastelaro, VR, Siqueira, Franco, Picone, C, Prediger, P. 2020. Effective removal of basic dye onto sustainable chitosan beads: Batch and fixed-bed column adsorption, beads stability and mechanism. *Sustainable Chemistry and Pharmacy*; 18:100348.

10. Xu, MY, Jiang, HL, Xie, ZW, Li, ZT, Xu, D, He, FA. 2020. Highly efficient selective adsorption of anionic dyes by modified β-cyclodextrin polymers. *Journal of the Taiwan Institute Chemical Engineers*; 108:114–28.

11. Basu, A, Suresh, Kumar G. 2015. Thermodynamics of the interaction of the food additive tartrazine with serum albumins: A microcalorimetric investigation. *Food Chemistry*; 175:137–42.

12. Vidal, M, Garcia-Arrona, R, Bordagaray, A, Ostra, M, Albizu, G. 2018. Simultaneous determination of color additives tartrazine and allura red in food products by digital image analysis. *Talanta*; 184:58–64.

13. Amsaraj, R, Mutturi, S. 2020. Real-coded GA coupled to PLS for rapid detection and quantification of tartrazine in tea using FT-IR spectroscopy. *Lwt Food Science and Technology;* 2020:110583.

14. Drzeżdżon, J, Jacewicz, D, Sielick,a A, Chmurzyński, L. 2019. A review of new approaches to analytical methods to determine the structure and morphology of polymers. *TrAC - Trends in Analytical Chemistry*; 118:470–6.

15. Ng, HM, Saidi, NM, Omar, FS, Ramesh, K, Ramesh, S, Bashir, S. 2018. Thermogravimetric Analysis of Polymers. *Encyclopedia of Polymer Science and Technology,* 2018:1–29.

16. Ahmad, MA, Ahmad, Puad, NA, Bello, OS. 2014. Kinetic, equilibrium and thermodynamic studies of synthetic dye removal using pomegranate peel activated carbon prepared by microwave-induced KOH activation. *Water Resources and Industry*; 6:18–35.

17. Yan, YZ, Nagappan, S, Yoo, JM, Nechikkattu, R, Park, SS, Ha, CS. 2020. Polyethyleneimine-grafted polysilsesquioxane hollow spheres for the highly efficient removal of anionic dyes and selective adsorption of Cr(VI). *Journal of Environmental Chemical Engineering* 2020:104814.

18. Alrobei, H, Prashanth, MK, Manjunatha, CR, Kumar, CBP, Chitrabanu, CP, Shivaramu, PD, Kumar, KY, Raghu, MS. 2021. Adsorption of anionic dye on eco-friendly synthesised reduced graphene oxide anchored with lanthanum aluminate: Isotherms, kinetics and statistical error analysis. *Ceramic International;* 47(7): 10322-10331.

19. Bensalah, H, Younssi, SA, Ouammou, M, Gurlo, A, Bekheet, MF. 2020. Azo dye adsorption on an industrial waste-transformed hydroxyapatite adsorbent: Kinetics, isotherms, mechanism and regeneration studies. *Journal of Environmental Chemical Engineering*; 8:103807.

20. Chen, H, Deng, X, Ding, G, Qiao, Y. 2019. The synthesis, adsorption mechanism and application of polyethyleneimine functionalized magnetic nanoparticles for the analysis of synthetic colorants in candies and beverages. *Food Chemistry*; 293:340–7.

21. Ghaedi, M, Sadeghian, B, Pebdani, AA, Sahraei, R, Daneshfar, A, Duran, C. 2012. Kinetics, thermodynamics and equilibrium evaluation of direct yellow 12 removal by adsorption onto silver nanoparticles loaded activated carbon. *Chemical Engineering Journal*; 187:133–41.

22. Bacioiu, IG, Stoica L, Constantin, C, Stanescu, AM. 2017. Removal of Tartrazine from Aqueous Solution by Adsorption on Activated Red Mud. *Water, Air& Soil Pollution;* 228.

23. Dakshene, M, Jain, R .2010. Adsorptive removal of tartrazine (E 102) over alkali activated fly ash. *Asian Journal of Chemistry;* 22:7733–7738.

24. Gautam, RK, Gautam, PK, Banerjee, S, Rawat, V, Soni, S, Sharma, SK, Chattopadhyaya, MC. 2015. Removal of tartrazine by activated carbon biosorbents of Lantana camara: Kinetics, equilibrium modeling and spectroscopic analysis. *Journal of Environmental and Chemical Engineering*; 3:79–88.

25. Banerjee, S., Chattopadhyaya, M. C. 2017. Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product. *Arabian Journal of Chemistry;* 10: S1629–S1638.

26 Goscianska, J, Pietrzak, R. 2015. Removal of tartrazine from aqueous solution by carbon nanotubes decorated with silver nanoparticles. *Catalysis Today*; 249:259–264