

Investigation of Adsorption Isotherm Models for Interaction of P(AAm-CIAETA) and Carminic Acid, and Theoretical Approaches

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ABSTRACT

In this study, the adsorption isotherm models for the sorption of carminic acid on P(AAm-CIAETA) hydrogels are explained by experimental and theoretical studies. The crosslinked hydrogels with ethylene glycol dimethacrylate were prepared by radical addition reaction of acrylamide (AAm) and 2-(acryloyloxy)ethyl trimethylammonium chloride (CIAETA) monomers in an aqueous solution. The spectral and morphological analyses of P(AAm-CIAETA) hydrogels were performed by FTIR/ATR and SEM, respectively. The adsorbed amounts of carminic acid on P(AAm-CIAETA) hydrogels were evaluated by Giles, Langmuir, and Freundlich adsorption isotherm models. Langmuir parameters were calculated for the adsorption of the dye on the hydrogels according to the L-type Giles isotherm. In addition, it was determined that its adsorption was appropriate from the RL values calculated for 500 mg L⁻¹ carminic acid concentration. In addition, molecular electrostatic potential (MEP) mapping was performed to predict the reactive sites of P(AAm-CIAETA) hydrogels and carminic acid. The results showed that the theoretical and experimental data of the hydrogels were in agreement with each other. As a result, it can be said that P(AAm-CIAETA) hydrogels are suitable for the removal of anionic dyes such as carminic acid from aqueous solutions.

Keywords: 2-(acryloyloxy)ethyl trimethylammonium chloride, Acrylamide, Hydrogel, Carminic acid, Molecular electrostatic potential (MEP).

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Introduction

Pollution from dyes has been and continues to be a major global problem due to their toxicity. Dyes, which are used in large quantities as colorants in paper, printing and textiles, plastics and paints, excessively pollute domestic and agricultural waters. A paramount variety of adsorbents have been used, manufactured and designed to remove these pollutants [1-10].

Although there are many studies on dye removal with these adsorbents, there are fewer studies on the removal of anionic dyes compared to cationic dyes.

Carminic acid (E120), which is widely used in textile, cosmetic, printing, food, medical, and pharmaceutical applications [4], is a red anionic natural dye derived from *Dactylopius coccus* species and the insect known as the cochineal beetle [2,3]. In addition, carminic acid is the dye that gives color to cola, which is consumed worldwide in thousands of tons per day. According to the World Health Organization (WHO), carminic acid is considered safe at concentrations as low as 0.005 mg L⁻¹. At higher intakes, it is a toxic and neurotoxic dye that can cause skin and eye diseases and cancer [5].

In the literature, some adsorbents such as 4.03 mg g⁻¹ on glass powder [2], 33.44 mg g⁻¹ on (CuAl-CLDH/CNT/PVDF400) composites [3], 10.10 mg g⁻¹ on activated carbon [5], 48.5 mg g⁻¹ on mesoporous carbon

[6], 148 mg g⁻¹ on *Prunus mahaleb* bark [7] have been reported to be used for removal of carminic acids.

The adsorbents used in environmental applications to remove various harmful pollutants such as dyes from the water system are desired to be environmentally friendly and cost-effective [8-10]. Functional hydrogels are the adsorbents that best meet this desire.

The aim of this study was to prepare synthetic acrylamide-based functional hydrogels, which are different from the natural and natural product-derived adsorbents such as glass powder, carbon-based, and plant shell-based reported in the literature, and to use them for anionic dye removal. 2-(Acryloyloxy) ethyl trimethylammonium chloride (CIAETA) containing functional groups such as a quaternary ammonium group desired for carminic acid removal, an anionic dye, and acrylamide (AAm) monomers that increase mechanical strength were copolymerized in the presence of a crosslinking agent. The removal of carminic acid from the prepared P(AAm-CIAETA) was determined to be L-type according to the Giles adsorption isotherm classification by Freundlich isotherm, and the removal performance was evaluated using the Langmuir adsorption isotherm model.

Materials and Methods

Materials

Acrylamide (AAm), ethylene glycol dimethacrylate (EGDMA), ammonium persulfate (APS) were purchased from Merck Company (Germany). 2-(Acryloyloxy)ethyl trimethylammonium chloride (CIAETA), N, N, N', N'-tetramethylethylenediamine (TEMED) were purchased from Sigma Aldrich (USA). Double-distilled water was used in all experiments.

Synthesis of Hydrogels

8.0 mol of AAm and 2.0 mol of CIAETA monomers and 0.5 mol of EGDMA were dissolved in water, 0.01 mol of APS as initiator and 0.01 mol of TEMED as accelerator were added and filled into plastic pipettes. The gelled samples were removed from the pipettes, cut into 3-4 mm pieces, washed with double-distilled water, dried and named P(AAm-CIAETA).

Characterization of Hydrogels

Bruker Tensor II and Tescan-Mira 3 were used to obtain FTIR/ATR spectra and SEM images of the hydrogels, respectively.

Adsorption Studies

The adsorption of carminic acid in the range of 10-500 mg L⁻¹ on P(AAm-CIAETA) hydrogels was investigated by keeping it in a shaker at 25 °C for 24 hours. The equilibrium concentrations of carminic acid were determined by Shimadzu A160 model UV-VIS.

Results and Discussion

Synthesis of Hydrogels

The feed composition of copolymer hydrogels affects their performance in the field of application. In this study, P(AAm-CIATA) hydrogels were prepared by adding CIAETA comonomer containing ionizable groups to AAm monomer, which is inexpensive and has high mechanical strength but is neutral. As a result of preliminary experiments, the feed composition of P(AAm-CIATA) hydrogels was determined to be AAm:CIAETA = 8:2. The use of higher amounts of CIAETA caused the hydrogels to disintegrate.

P(AAm-CIAETA) hydrogels were prepared by a free radical addition reaction in the presence of EGDMA, and the plausible polymerization mechanism is shown in Figure 1.

In an aqueous medium, hydroxyl and/or sulfate radicals were formed from the initiator. These radicals then led to the copolymerization of AAm and CIAETA and their crosslinking with EGDMA [8-10].

The hydrogels prepared in a cylindrical structure were hard when dry and soft when swollen. The hydrogels maintained the cylindrical geometry in the dry and swollen states.

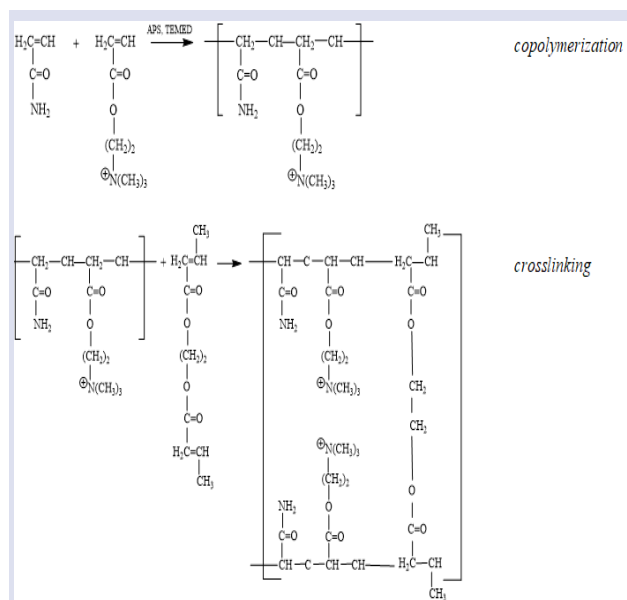


Figure 1. Plausible copolymerization/crosslinking mechanism of P(AAm-CIAETA).

Characterization of hydrogels

The spectroscopic examinations necessary to elucidate the chemical structures of the P(AAm-CIAETA) hydrogels before and after adsorption was performed with FTIR/ATR spectrophotometer, and the FTIR/ATR spectra are presented in Figure 2.

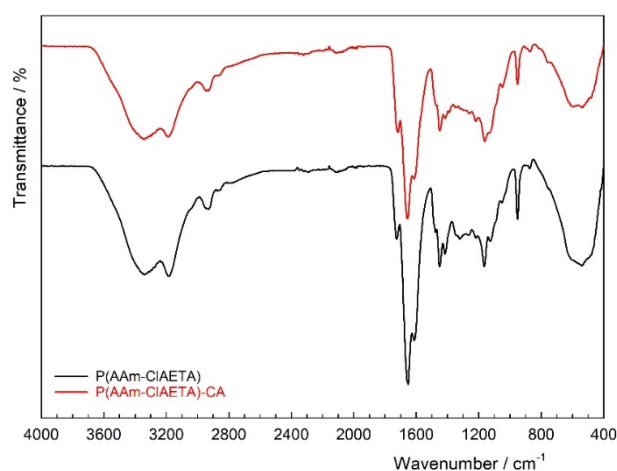


Figure 2. The FTIR/ATR spectrum before and after carminic acid adsorption onto the hydrogels

The bands at 3200-3600 cm⁻¹ are the N-H stretching vibration of the amide group. The C-N stretch of the quaternary ammonium (N⁺-(CH₃)₃) groups in the CIAETA monomer is observed at 1476 cm⁻¹ and the -CH bending of the ammonium methyl groups is observed at 952 cm⁻¹. The bands at 1729 cm⁻¹ and 1655 cm⁻¹ are considered to belong to the carbonyl group (C=O) in the crosslinker with the CIAETA monomer. In addition, the bands at 1162 cm⁻¹ and 1042 cm⁻¹ belong to the asymmetric and symmetric stretching vibration of the ester bond C-OC- in the CIAETA monomer. The FTIR/ATR spectral results

show the interactions between the hydrogels and dye molecules due to the decrease in density in characteristic bands such as C=O, N⁺-(CH₃)₃, and C-OC- of the hydrogels after adsorption [11-14].

The plausible mechanism of interaction between P(AAm-CIAETA) hydrogels and carminic acid is presented in Figure 3.

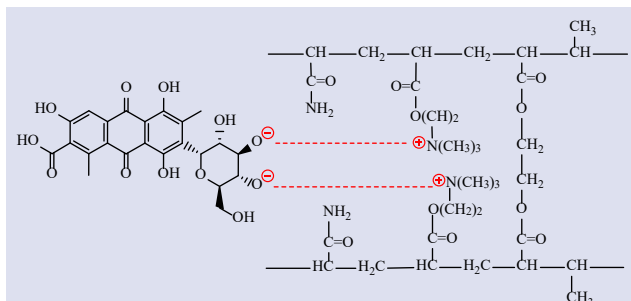


Figure 3. Plausible mechanism of interaction between the hydrogels and carminic acid.

The main interactions between the hydrogels and anionic dye may be electrostatic interactions, dipole-dipole interactions, hydrogen bonds, and hydrophobic interactions. Especially, electrostatic interactions will be expected between hydroxyl groups on the dye molecules and -N⁺(CH₃)₃ on the hydrogels.

SEM images of P(AAm-CIAETA) hydrogels, photos of carminic acid solution before/after adsorption, and photos of P(AAm-CIAETA) hydrogels before/after adsorption are presented in Figure 4.



Figure 4. (a) SEM images of the hydrogels, (b) photos of carminic acid solution before/after adsorption, (c) photos of dried the hydrogels before/after adsorption.

SEM images show that the hydrogels have a smooth and regular surface morphology. It is also seen that the cavities on the surface of the hydrogels are homogeneous [8].

From Figure 4. b-c, it can be seen that the color of P(AAm-CIAETA) hydrogels kept in carminic acid solution changed to red. This indicates that P(AAm-CIAETA) hydrogels interact with carminic acid and can be used for removal from an aqueous solution.

Adsorption Studies

For the adsorption equilibrium, the total dye concentration (C , mg L⁻¹) is:

$$C = C_b + C_e \quad (1)$$

C_e and C_b are the equilibrium concentration of the dye in the solution and hydrogels (mg L⁻¹), respectively. The amount of adsorbed dye (q , mg g⁻¹) on 0.1 g hydrogel from 50 mL carminic acid solutions was calculated by Equation 1, 2.

$$q = (C_b \cdot V) / m \quad (2)$$

The adsorption of carminic acid on the hydrogels was investigated with the Giles, Langmuir, and Freundlich adsorption isotherm models [8,15,16].

Adsorption isotherms were constructed by calculating the amount of dye adsorbed from carminic acid solutions onto the hydrogels in the concentration range of 10-500 mg L⁻¹ and are shown in Figure 5 [8,9,15].

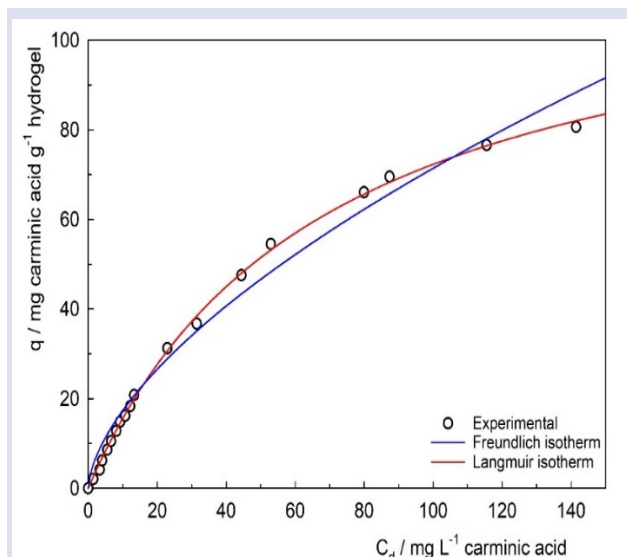


Figure 5. Carminic acid adsorption isotherms on the P(AAm-CIAETA) hydrogels.

According to the isotherms classified by Giles as S (sigmoidal), L (Langmuir), H (high affinity) and C (constant distribution), the adsorption isotherms of carminic acid on P(AAm-CIAETA) hydrogel resemble L-type curves [15].

The adsorption parameters calculated from the nonlinear equations of the graphs presented in Figure 5 are summarized in Table 1.

Table 1. Isotherm parameters of carminic acid adsorption on P(AAm-CIAETA) hydrogels

Models	Equations	Values
Freundlich		
	$q = X_F C_d^{1/n}$	
Freundlich constant, K_F [(mg g ⁻¹)(L mg ⁻¹) ^{1/n}]		4.21
Heterogeneity factor, n		1.63
Correlation coefficient, r		0.991
Isotherm type		L-type
Langmuir		
	$q = \frac{X_L K_L C_d}{1 + K_L C_d}$	
Monolayer adsorption capacity, X_L (mg g ⁻¹)		120.9
Distribution coefficient, K_L (L mg ⁻¹)		0.015
Correlation coefficient, r		0.999
Adsorbent dose, AD_L (g L ⁻¹)	$AD_L = \frac{C - C_e}{q}$	4.45
Dimensionless dispersion factor, R_L	$R_L = \frac{1}{1 + K_L C}$	0.117

In addition, the type of isotherm can be determined from the n value found in the Freundlich isotherm model. At the same time, the n values are related to the Giles classification, S-, L-, and C-type isotherms. $n < 1$ corresponds to S-type, $n = 1$ to C-type, and $n > 1$ to L-type. The Freundlich constant for the P(AAm-CIAETA) hydrogel was $n > 1$, indicating that the isotherm type is L-type. The L-type isotherm curve indicates a strong intermolecular interaction between carminic acid and the P(AAm-CIAETA) hydrogel. On the other hand, higher values of K_F represent easy adsorbate uptake from the solution [16].

In order to determine the suitability of adsorption, the R_L value for removal from the dye solution with an initial concentration of 500 mgL⁻¹ was calculated as 0.117. This R_L value shows that carminic acid adsorption on P(AAm-CIAETA) is in the range of suitability [8,10].

The adsorbent dose required for 50 % removal from 500 mg L⁻¹ carminic acid solution was calculated as $AD_L = 4.45$ g L⁻¹. This result shows that P(AAm-CIAETA) hydrogels are effective in carminic acid removal and can be easily used.

The maximum adsorption capacities of previous studies on carminic acid adsorption on various adsorbents are presented in Table 2 and compared with the results of this study.

Table 2 shows that the amount of carminic acid adsorbed by P(AAm-CIAETA) hydrogels is 2.5 to 30 times higher compared to previously studied adsorbents (except Prunus mahaleb shell).

Table 2. The maximum adsorption capacities of some adsorbents for carminic acid adsorption

Adsorbent	Maximum adsorption capacities/mg g ⁻¹	References
glass powder (GP)	4.03	[2]
carbon nanotubes/polyvinylidene fluoride	33.44	[3]
(CuAl-CLDH/CNT/PVDF400) composite	10.10	[5]
activated carbon	48.50	[6]
mesoporous carbon	148.00	[7]
Prunus mahaleb shell	120.90	In this study

There are 667526 adsorption studies in the Web of Science (WOS) database since 1970. 38 of these studies are related to carminic acid adsorption on different natural and natural product-derived adsorbents [17]. As a result of the evaluations, this study can be recommended as a pioneering study for the use of polymeric structures, especially hydrogels, in the excellent removal of carminic acid.

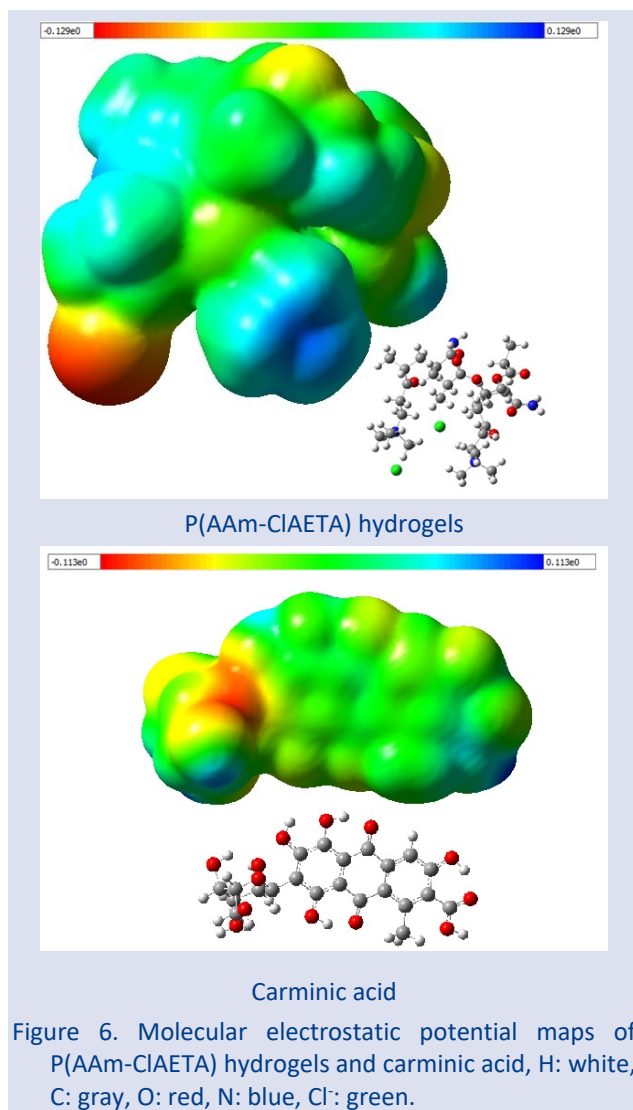
Molecular Electrostatic Potential Map

The molecular electrostatic potential (MEP) is widely used in the qualitative evaluation of the chemical reactivity of surfaces with molecular electron density. The nucleophilic (electron-poor) and electrophilic (electron-rich) regions of the molecule are determined by MEP maps. In the MEP map, electrophilic regions are shown in red and nucleophilic regions in blue. In MEP maps, the electrostatic potential increases in the order of Red<Orange<Yellow<Green<Blue. Green-colored regions in MEP maps indicate neutral regions and blue-colored regions indicate nucleophilic regions. With the help of these colors, charge distributions on the molecular surface, plausible electrostatic interaction regions, and electrophilic and nucleophilic regions are determined [18-20].

In this study, it was aimed to determine the active sites in the molecular structure of P(AAm-CIAETA) hydrogels and carminic acid by using MEP maps and to evaluate plausible interaction sites with each other.

Molecular simulation calculations were done using Gaussian 16 AML64L-Revision-C.01 [21] and visualization of results using GaussView 6.0 [22]. The molecular structures of the repeating units of the hydrogels were optimized using density functional theory (DFT) with the Lee-Yang-Parr non-local correlation functional (B3LYP) using 6-31G (d,p) basis set [23-25].

Molecular electrostatic potential maps of P(AAm-CIAETA) hydrogels and carminic acid are presented in Figure 6.



When MEP maps were examined, the following conclusions and evaluations were reached [18-20].

✓ In the MEP map of the P(AAm-CIAETA) hydrogels, the regions with the quaternary ammonium $[N^+-(CH_3)_3]$ group are shown in blue, these regions are the nucleophilic attack regions.

✓ The regions of hydroxyl groups attached to the tetrahydropyran ring in the carminic acid molecules are shown in red, these regions are the electrophilic attack regions.

According to these results, it can be said that the electrostatic interactions between the quaternary ammonium groups of the P(AAm-CIAETA) hydrogels and the hydroxyl groups attached to the tetrahydropyran ring in the carminic acid molecules are stronger and more likely. This evaluation with MEP maps supports the proposed plausible interaction mechanism between P(AAm-CIAETA) hydrogels and carminic acid, presented in Figure 3.

Conclusions

The crosslinked P(AAm-CIAETA) hydrogels were prepared by free radical addition polymerization. The absence of any change in the FTIR spectra taken before

and after adsorption indicated that the hydrogel-carminic acid interactions were physical. According to the MEP maps, electrostatic interactions between the quaternary ammonium groups of P(AAm-CIAETA) hydrogels and the hydroxyl groups attached to the tetrahydropyran ring in carminic acid molecules are stronger and more likely. The adsorption of carminic acid on P(AAm-CIAETA) hydrogels was determined to be L-type according to Giles adsorption isotherms classification. In addition, the heterogeneity factor $n=1.63$ calculated from the Freundlich isotherm model supported the L-type adsorption isotherm. The monolayer adsorption capacity was calculated as 120.9 mg g^{-1} from the Langmuir isotherm model. It was determined that carminic acid adsorption on P(AAm-CIAETA) hydrogels were favorable, and the adsorbent dose value was $AD_L=4.45 \text{ g L}^{-1}$.

According to these results, it can be said that P(AAm-CIAETA) hydrogels can be used in carminic acid removal.

Acknowledgments

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Conflicts of interest

There are no conflicts of interest in this work.

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