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Synthesis and Characterization of Cationic P(AAm-AETAC) Hydrogels, and Their Uses in Adsorption of Titan Yellow

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ABSTRACT

In this study, a new cationic P(AAm-AETAC) hydrogels were prepared by a radical addition reaction in aqueous solution with acrylamide and [2-(acryloyloxy)ethyl] trimethylammonium chloride) comonomers in the presence of ethylene glycolmethacrylate. Hydrogels were characterized by spectroscopic, surface, and thermal analysis. The hydrogel does not undergo any structural degradation with the effect of heat up to 250 °C.

The adsorption of titan yellow from aqueous solution to the newly prepared cationic hydrogels was evaluated by Freundlich, Langmuir, and Temkin isotherms. The dye adsorption to hydrogels prepared from adsorption isotherms was L type according to the Giles adsorption isotherms. It was determined that the adsorption of titan yellow to the hydrogels prepared from the R_L values calculated for a concentration of 500 mg L^{-1} titan yellow was favorable. The dye removal efficiency of the hydrogel from the aqueous solution was found to be about 98%. As a result, it can be said that the cationic P(AAm-AETAC) hydrogel, which is prepared at a low cost, can provide a high amount of removal in the adsorption of anionic dyes from aqueous solutions.

Keywords: [2-(acryloyloxy)ethyl] trimethylammonium chloride, Acrylamide, Hydrogel, Titan yellow, Adsorption.

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Introduction

Water is the most important life component for all living things. Due to the increase in global warming and desertification, the amount of water has become a concern in the world. Population development, rapid industrialization, and inappropriate use of natural water cause serious concerns about the amount and quality of water per capita.

Water pollution is the mixing of unwanted harmful substances in water that can degrade the quality of the water in a measurable amount. Houses, industrial establishments, thermal power plants, fertilizers and chemical pesticides, agricultural industry wastewater, hot water, and substances from nuclear power plants are the main sources of water pollution.

Dyes, which are one of the common water pollutants left by the food, leather, and textile industries, color the water to a great extent even at concentrations as low as 1 ppm. This coloration not only causes an unwanted change in water quality in terms of aesthetic properties but also directly or indirectly affects human and living things' health. Its effects may be in the forms of carcinogenicity, mutagenicity, poisoning, and metabolism in water bodies [1].

Various physical and chemical methods such as flocculation/coagulation, adsorption, and chemical oxidation can be used for the treatment of wastewater. The fact that the removal efficiency varies depending on the type and amount of the pollutant in the wastewater makes it more difficult to choose the most appropriate method for removal from wastewater.

The adsorption process is one of the most common and effective methods of removing contaminants. Although the most commonly used adsorbent is activated carbon, some easy-to-produce and cheap adsorbents such as zeolite, bentonite, and wood ash are also used for removal. In recent years, studies with composite materials or artificial adsorbents have attracted attention. In particular, cross-linked, networked hydrogels containing functional groups such as amine, hydroxyl, carboxyl, and sulfonyl are used as adsorbents to remove contaminants from aqueous solutions [2,3].

It is an organic triazine azo dye that is widely used in dyeing Titan yellow, nylon, and wool and in some microscopic examinations. El-Azazy et al. studied the removal of Titan yellow with a green adsorbent recycled from Aloe vera leave waste. As a result of their adsorption studies, they found the maximum adsorption capacity of 55.25 mg g^{-1} with the Langmuir equation [1].

Cheng et al. Prepared a positively charged microporous ceramic membrane and used it for titan yellow removal. The positively charged microporous ceramic membrane exhibited a flow rate of 421 L m^{-2} hours at a trans-membrane pressure of 0.03 bar. They also stated that between pH 3-8, Titan yellow can be effectively removed with 10 mg L^{-1} feed concentration [4].

Ghaemi et al. determined the adsorption properties (pH, dye concentration, adsorbent amount, interaction time, ionic

strength, and temperature) of Titan yellow and Congo red from aqueous solution on $CoFe_2O_4$ magnetic nanoparticles and found the maximum adsorption capacity as 212.8 mg g^{-1} [5].

Dyes, one of the major causes of water pollution, can be anionic, cationic, or amphoteric. There are fewer studies on the removal of anionic dyes than cationic dyes, although they pollute the environment equally.

There are 602738 adsorption studies since 1970 in the Web of Science (WOS) database. 32 of these studies are related to cationic hydrogels and only 11 of them studied dye adsorption. This evaluation on WOS shows the importance of the P(AAm-AETAC) hydrogel prepared in this study for anionic dyes adsorption [6].

In this study, it was aimed that the synthesis and characterization of cationic P(AAm-AETAC) hydrogel with acrylamide and [2-(acryloxy) ethyl] trimethylammonium chloride monomers and its use in the adsorption of titan yellow.

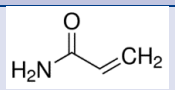
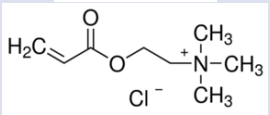
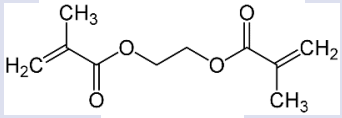
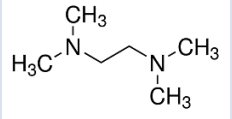
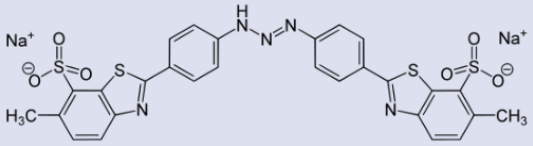
Materials and Methods

Materials

Acrylamide (Merck, Germany) and [2-(acryloyloxy) ethyl] trimethylammonium chloride (Sigma, USA) as monomers, ethylene glycol dimethacrylate (Merck, Germany) as crosslinkers, ammonium persulfate (Merck, Germany) as initiator, N, N, N', N'-tetramethylethylenediamine (Sigma, USA) as accelerator were analytical grade and were used as received. Titan yellow was purchased from Merck (Germany).

The structures of the chemicals used in the study are presented in Table 1.

Table 1. The structures of the chemicals

Chemicals	Representation	Chemical structure
Acrylamide	AAm	
[2-(acryloyloxy) ethyl] trimethylammonium chloride	AETAC	
Ethylene glycol dimethacrylate	EGDMA	
Ammonium persulfate	APS	$(NH_4)_2S_2O_8$
N,N,N',N'-tetramethylethylenediamine	TEMED	
Titan yellow	TY	

Synthesis of Hydrogels

Acrylamide (AAm; 0.8 mol), [2- (acryloyloxy) ethyl] trimethylammonium chloride (AETAC; 0.2 mol) and ethylene glycolmethacrylate (EGDMA; 0.05 mol) were dissolved in water. Then 0.001 mol ammonium persulfate and 0.001 mol N, N, N ', N 'tetramethylethylenediamine were added. The mixture was placed into PVC straws. After 24 hours, the hydrogels were removed from the straws, cut into pieces 2-3 mm in length, washed with distilled water, and then dried in air and vacuum. The hydrogels were shown as P(AAm-AETAC) and used in powder form.

Characterization

FTIR/ATR spectra of hydrogels were taken with a Bruker Tensor II model spectrophotometer in the 4000-400 cm^{-1} range. SEM images of hydrogels at various magnifications were taken with Tescan-Mira 3 brand Scanning Electron Microscope (SEM). TG thermograms of hydrogels were taken with Shimadzu TG-60 model thermal analyzer. Thermal tests were performed using a sample mass of 5-10 mg under a nitrogen atmosphere at a scan rate of 10 ^oC min^{-1}.

Adsorption Studies

To examine the concentration effect, 0.1 g P(AAm-AETAC) hydrogels were added to 50 mL of titan yellow solutions in the range of 50-500 mg L^{-1} and kept in a shaker at 25 ^oC for 24 hours and the equilibrium concentrations were determined. During the adsorption studies, the concentration of titan yellow solutions was recorded at wavelengths of 403 nm, using a Shimadzu A160 model UV-VIS spectrophotometer.

Results and Discussion

Synthesis of Hydrogels

The cationic hydrogels composed of AAm and AETAC were prepared by free radical solution polymerization in the presence of a crosslinker and the possible polymerization mechanism is presented in Figure 1.

In polymerization, the first step is a reaction between APS and TEMED. The activated TEMED molecule can combine with monomers or crosslinker molecules; in the process, the unpaired electron is transferred to the monomeric units so that they, in turn, become reactive. The polymer can continue growing indefinitely, with the active center being continually shifted to the free end of the chain. After 24 h, the hydrogels were cut into pieces of 2–3 mm length, washed with distilled water, and dried.

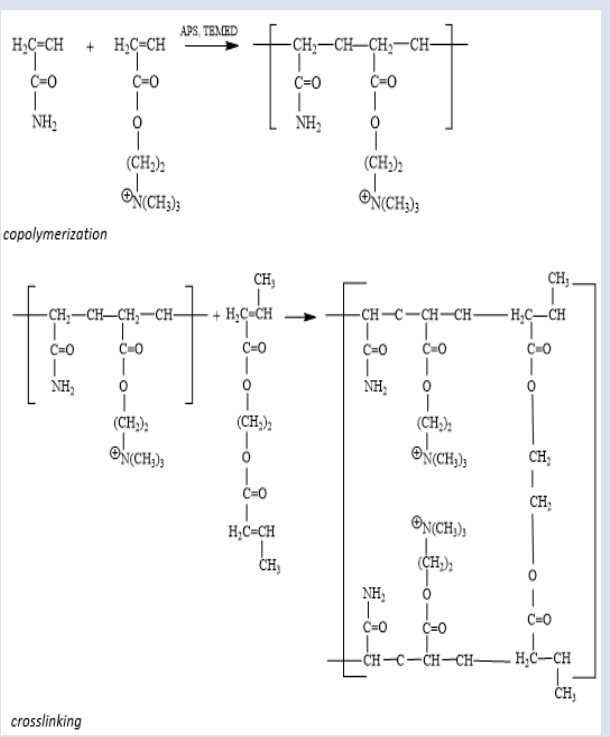


Figure 1. Possible polymerization mechanism of P(AAm-AETAC)

Characterization

FTIR/ATR analysis

ATR spectra of P(AAm-AETAC) hydrogels are presented in Figure 2. The characteristic vibrational bands of the functional groups are as observed: N-H stretch vibration of the amide group at 3200-3600 cm^{-1}, N-H bending vibration in amide structure at 1550 cm^{-1}, C=O stretch vibration in ester structure at 1729 cm^{-1} and $-N^{+}(CH_3)_3$ bending band of the quaternary ammonium pending group at 1476 cm^{-1}. The absence of bands at 900-1000 cm^{-1}, which is evidence of monomeric double bonds, indicates that AAm and AETAC monomers have polymerized successfully [2].

In Figure 2, the presence of new peaks at 1040, 1088, and 1198 cm-1, displacement or variation in peak intensity indicates that the dye molecules are related to the hydrogels [7].

The main interactions between the hydrogel and anionic dye may be electrostatic and hydrophobic.

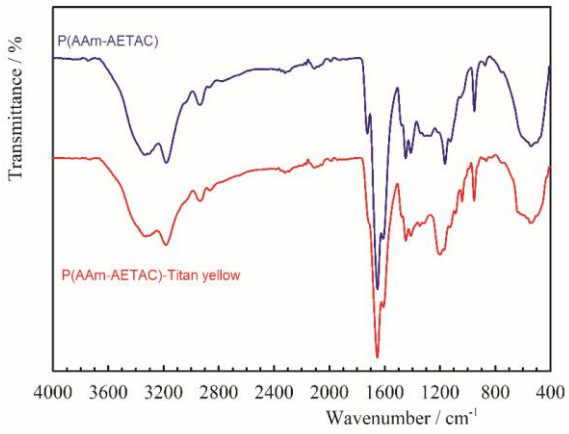


Figure 2. ATR spectra of P(AAm-AETAC) hydrogels.

The possible mechanism of interaction between P(AAm-AETAC) hydrogels and titan yellow is presented in Figure 3.

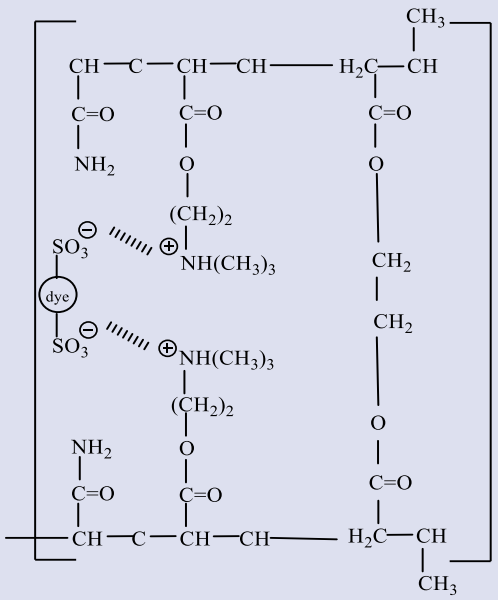


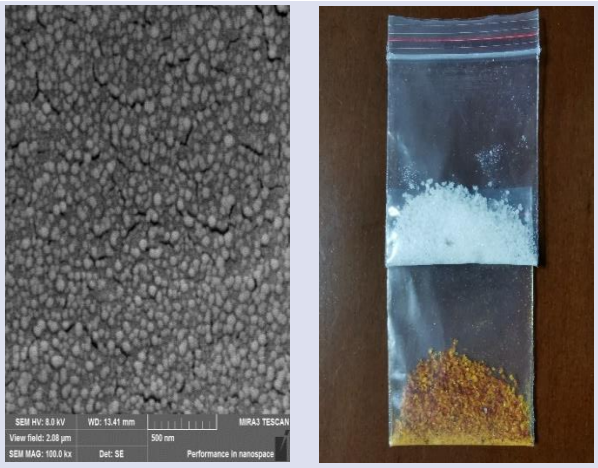
Figure 3. Possible mechanism of interaction between P(AAm-AETAC) hydrogels and titan yellow.

Especially, electrostatic interactions will be expected to occur between $-SO_3^-$ groups on the dye molecules and $-N^{+}(CH_3)_3$ on the monomer unit of the crosslinked polymer.

Hydrophobic effects occur especially in aqueous solution interactions which in the present case will involve aromatic rings on the dye molecules and the methyl groups on the gel. There can be some other interactions such as dipole-dipole and dipole-induced dipole interactions between the dye molecules and the hydrogel chains.

SEM images

SEM images and photographs of the prepared P(AAm-AETAC) hydrogels are presented in Figure 4.



a b

Figure 4. (a) SEM images of P(AAm-AETAC) hydrogels, (b) photographs of hydrogels before and after adsorption.

In the SEM image presented in Figure 4a, it is seen that P(AAm-AETAC) hydrogels have a regular surface structure, there are gaps on the surface of the polymer and these spaces are homogeneous. In the photograph presented in Figure 4b, white-colored P(AAm-AEAC) hydrogels turned brownish-yellow after the dye adsorption.

Thermal analysis

TG and DTA thermograms of P(AAm-AETAC) hydrogels were taken to determine their thermal properties and are presented in Figure 5.

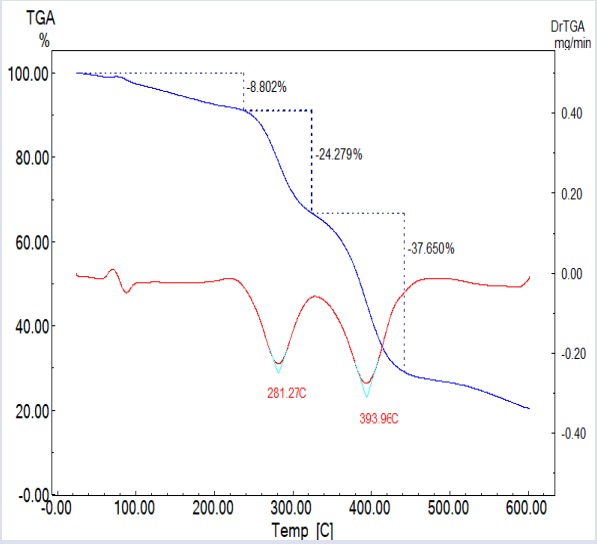


Figure 5. TG thermograms of P(AAm-AETAC) hydrogels.

The initial degradation temperature (T_i), the temperature at the degradation maximum rate (T_m), the degradation final temperature (T_f), the maximum degradation rate (r_m), the residual mass (C_m) at the maximum rate, and the residual mass (C_r) at the end of degradations are given Table 2.

Table 2. Thermogravimetric parameters of P(AAm-AETAC) hydrogels

Degradation region	T_i/°C	T_m/°C	C_m/%	T_f/°C	r_m/mg min^{-1}	C_r/%
1	235	281	79.15	325	0.28	66.36
2	325	393	45.66	440	0.07	28.88

In the TG thermogram of P(AAm-AETAC) given in Figure 5, three different regions are seen such as evaporation of moisture, separation of side groups attached to the main chain due to intramolecular and intermolecular reactions of side groups, and main chain scission. The first stage (25–235°C, 8.802% mass loss) was attributed to the evaporation of moisture from the adsorbed and bound water. The second step (235–325°C, 24.279% mass loss) was attributed to the thermal decomposition of methyl in quaternary ammonium groups as well as the imine reaction of the amide group. The third stage of mass loss occurred at the following intervals. 325–440 ^{0}C for P(AAm-AETAC) with approximately 37.65% mass loss from thermal decomposition of the copolymer backbone [8, 9]. It is seen that 50 % of the hydrogels degrade at 387 °C (the half-life temperature, T_h). In addition, 19.71% of P(AAm-AETAC) was found as residue at 600 °C.

Adsorption Studies

In an adsorption system at equilibrium, the total titan yellow concentration (C, mg L^{-1}) can be given as:

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

$$Q = \frac{C_b . V}{m} \quad (2)$$

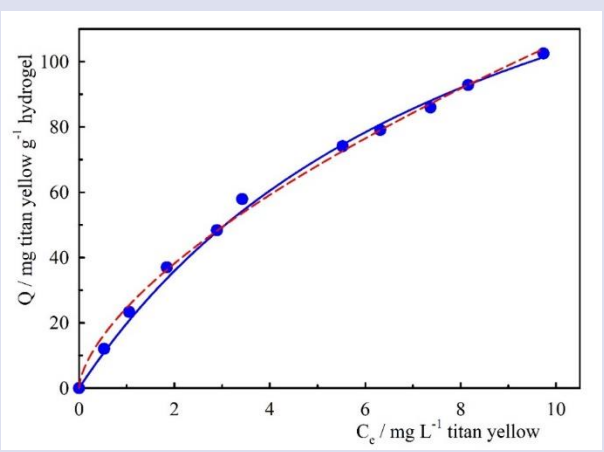
C_b is the equilibrium concentration of titan yellow on the hydrogel (mg L^{-1}) and C_e is the equilibrium concentration of titan yellow in solution (mg L^{-1}). V is the volume of the solution (L) and m is the mass of the hydrogels (g). The amount of substance (Q) adsorbed on the hydrogels was calculated by Equations 1 and 2.

Adsorption isotherm models

The adsorption of a solute from solution to a solid is usually given according to the Giles adsorption isotherm classification. With the Freundlich isotherm model, the type of adsorption (such as S, L, C) and if it is type L, the monolayer adsorption capacity, distribution coefficient, dimensionless dispersion factor, adsorbent dose, and removal efficiency values can be calculated with the Langmuir isotherm model. In addition, with the Temkin isotherm model, adsorption energy change and Temkin equilibrium constant values can be determined. Figure 6 was created for the adsorption of titan yellow in the concentration range of 50-500 mg L^{-1} on P(AAm-AETAC) [2,10,11].

The parameters of Freundlich, Langmuir, and Temkin isotherm models and derivated parameters are calculated

from the nonlinear regression of the plots in Figure 6, and have been summarized in Table 3.



: Langmuir; --------: Freundlich isotherm.

Figure 6. Isothermal curves of titan yellow adsorption in P(AAm-AETAC) hydrogel.

The n values of the Freundlich isotherm model are related to the Giles classification, S, L, and C type isotherm. n < 1 correspond to S shape, n=1 C type, and n > 1 to L type [12]. On the other hand, higher values of K_F represent an easy uptake of adsorbate from the solution. The Freundlich exponent n for the P(AAm-AETAC) hydrogel is 1.58, thus suggesting an L-type isotherm. The most characteristic feature of L-type adsorption curves is that the adsorbed molecules have strong intermolecular interactions with the adsorbent.

The Q_m value in the Langmuir isotherm model was calculated as 191.7 mg g^{-1}. It has been observed that the highest monolayer capacity among the organic adsorbents in the studies carried out to date [1,4,5,7].

The efficiency of P(AAm-AETAC) hydrogel for titan yellow adsorption was investigated with dimensionless dispersion factor (R_L) values depending on the initial concentration and the calculated R_L values for 500 mg L^{-1} dye concentration were 0.017. Since the calculated R_L value is $0 < R_L < 1$, it was determined that titan yellow adsorption onto the P(AAm-AETAC) hydrogel was favorable [3].

The adsorbent mass values required for 50% removal from the hypothetical solution containing 500 mg L^{-1} titan yellow and defined as the adsorbent dose were 4.84 g L^{-1}. The amount of adsorbent required for removal is important in terms of cost. From the calculated adsorbent dose value, it is seen that the synthesized cationic hydrogels will provide low-cost removal.

The titan yellow removal efficiency of the P(AAm-AETAC) hydrogel was found to be approximately 98% for all concentrations. This value shows that the P(AAm-AETAC) hydrogel removes the titan yellow with very high efficiency.

The adsorption energy in the Temkin isotherm model was found to be 15.24 kJ mol^{-1}. The b value of $0 < b < 100$ indicates that the adsorption is exothermic and occurs through physical interactions. This result supports the idea that this physical interaction between the prepared cationic P(AAm-AETAC) hydrogels and anionic titan yellow is due to electrostatic forces. [13,14].

Table 3. Isotherm models parameters for titan yellow adsorption onto P(AAm-AETAC) hydrogel

Models	Equations	Values
Freundlich	$Q = K_F C_e^{1/n}$	
Freundlich constant; K_F ((mg g^{-1})(L mg^{-1})$^{1/n}$)		24.62
heterogeneity factor; n		1.58
correlation coefficient; R		0.998
isotherm type		L-type
Langmuir	$Q = \frac{Q_m K_L C_e}{1 + K_L C_e}$	
monolayer adsorption capacity; Q_m (mg g^{-1})		191.7
distribution coefficient; K_L (L mg^{-1})		0.115
correlation coefficient; R		0.991
adsorbent dose; AD_L (g L^{-1})	$AD_L = \frac{C - C_e}{Q}$	4.84
dimensionless dispersion factor; R_L	$R_L = \frac{1}{1 + K_L C}$	0.017
removal efficiency; RE%	$RE\% = \frac{C_b}{C} x100$	98
Temkin	$Q = \left(\frac{RT}{b}\right) \ln(K_T C_e)$	
adsorption energy change, b (k J mol^{-1})		15.24
Temkin equilibrium constant, K_T (L mg^{-1})		2.09
correlation coefficient; R		0.983
adsorption type		physical
adsorption energy type		exothermic

The maximum adsorption capacities of some adsorbents are presented in Table 4 for comparison with previous studies on titan yellow adsorption.

Table 4. Maximum adsorption capacities of some adsorbents for titan yellow adsorption

Adsorbent	Maximum adsorption capacity	Reference
A green adsorbent recycled from aloe vera leave waste	55.25 mg g^{-1}	[1]
Positively charged ceramic membrane	99 % (removal efficiency)	[4]
$CoFe_2O_4$ magnetic nanoparticles	212.8 mg g^{-1}	[5]
polyaniline@SiO2 nanocomposite	141.5 mg g^{-1}	[7]
P(AAm-AETAC) hydrogel	191.7 mg g^{-1} 98% (removal efficiency)	In this study

It is seen that the prepared P(AAm-AETAC) hydrogels are quite good compared to the Aloe vera-based adsorbent used for titan yellow adsorption. In addition, the amount of adsorbed dye is very close to magnetic nanoparticles. In addition, P(AAm-AETAC) hydrogels provided approximately the same amount of dye removal as the positively charged ceramic membrane.

Conclusions

- ✓ P(AAm-AETAC) cationic hydrogel was prepared by a free radical addition reaction in the presence of crosslinker (EGDMA).
- ✓ Although P(AAm-AETAC) hydrogels are glassy in appearance and very hard when dry, they soften when inflated. The gels maintain the geometry of the cylindrical mold in a dry and swollen state.
- ✓ The absence of bands at 900-1000 cm^{-1}, which is evidence of monomeric double bonds, in the ATR spectrum of the P(AAm-AETAC) hydrogel showed that AAm and AETAC monomers were successfully polymerized.
- ✓ The absence of a change in the basebands of the ATR spectra before and after the adsorption of the hydrogel showed that the hydrogel-titan yellow interactions were physical.
- ✓ P(AAm-AETAC) hydrogel gives a two-step thermal decomposition reaction. However, it has been determined that the hydrogel does not undergo any structural deterioration under the influence of heat up to 250 °C and can be used easily up to this temperature.
- ✓ From the SEM image of the P(AAm-AETAC) hydrogel, it was seen that it has a very regular surface structure, there are local voids on the surface of the polymer and these voids are evenly distributed.
- ✓ While the neutral PAAm hydrogel and the anionic titan yellow did not interact, the adsorption of titan yellow was achieved with the [2-(acryloyloxy) ethyl] trimethylammonium chloride comonomer added to the structure.
- ✓ The value of n=1.58 calculated from the Freundlich isotherm proves that the isotherm of the titan yellow adsorption to the P(AAm-AETAC) hydrogel is L-type according to the Giles adsorption isotherms classification, and monolayer adsorption capacities were calculated from Langmuir curves.
- ✓ From the adsorbent dose values calculated from the Langmuir parameters, it was determined that the P(AAm-AETAC) hydrogel would provide the removal of the anionic titan yellow at low cost.
- ✓ It was determined from the R_L value calculated for the 500 mg L^{-1} titan yellow concentration that the adsorption of titan yellow in the P(AAm-AETAC) hydrogel was favorable.
- ✓ The titan yellow removal efficiency of the P(AAm-AETAC) hydrogel was found to be approximately 98%.
- ✓ From the values of the adsorption energy changes calculated from the Temkin isotherms, it was determined that the adsorption was exothermic and occurred with physical interactions.

As a result, it can be said that the prepared cationic P(AAm-AETAC) hydrogel can be used as a good adsorbent in the removal of anionic dyes from aqueous solutions and high removal can be achieved at low cost.

Conflicts of Interest

The authors declare no conflict of interest.

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