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Investigation of Photocatalytic Decolorization Parameters of Acid Violet 7 Dye With poly(ethylene glycol dimethacrylate-2-vinyl pyridine) -TiO_2 Photocatalytic Polymer Microbeads

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Photocatalytic polymer,
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Azo dye

Abstract: Poly(ethylene glycol dimethacrylate-2-vinyl pyridine)-TiO_2 [poly (EGDMA-2-VP)] - TiO_2 microbeads were synthesized by suspension polymerization method for photocatalytic decolorization of textile dyes from aqueous solution. The synthesized cross-linked [poly (EGDMA-2-VP)] - TiO_2 microbeads were characterized by scanning electron microscopy (SEM), X-ray Diffraction (XRD) and fourier transform infrared spectroscopy (FTIR). To investigate the usability of the obtained microbeads in dye decolorization, the paramreters such as pH, polymer amount, time, and dye concentration were examined both under sunlight and 366 nm UV light. Optimum conditions under which maximum photocatalytic decolorization of the dye were pH 3, polymer amount 0.05 g, dye concentration 30 mg /L and time 5 hours.

Poli(etilen glikol dimetakrilat-2-vinil piridin) -TiO_2 Fotokatalitik Polimer Mikro Küreleri ile Asit Violet 7 Boyasının Fotokatalitik Renk Giderme Parametrelerinin İncelenmesi

Anahtar Kelimeler
Fotokatalitik polimer,
Polimer mikroküreler,
Dekolorizasyon,
Azo boya

Özet: Poli(etilen glikol dimetakrilat-2-vinil piridin)-TiO_2 [poli(EGDMA-2-VP)] - TiO_2 mikro küreleri, tekstil boyar maddelerinin sulu çözeltiden fotokatalitik renk giderimi için süspansiyon polimerizasyon yöntemi ile sentezlendi. Sentezlenen çapraz bağlı [poli (EGDMA-2-VP)] - TiO_2 mikro küreleri, taramalı elektron mikroskobu (SEM), X-ışını difraktometresi (XRD) ve fourier dönüşümlü kızılötesi spektroskopisi (FTIR) ile karakterize edildi. Elde edilen mikro kürelerin boyar madde renk gidermede kullanılabilirliğini araştırmak için pH, polimer miktarı, zaman ve boya konsantrasyonu parametreleri, hem güneş ışığı altında hem de 366 nm UV ışığı altında incelendi. Boyar maddenin maksimum fotokatalitik renk gideriminin meydana geldiği optimum koşullar pH 3, polimer miktarı 0.05 g, boya konsantrasyonu 30 mg/L ve süre 5 saattir.

1. Introduction

The textile industry is one of the largest industries in the world that plays an important role in the economic activities of many countries. All the dye applied during the dyeing process is not fixed on the fabric and some of it is washed off. Unfixed dyes are in high concentration in textile wastewater. Therefore, a large amount of wastewater is released in the textile industry [1]. In the textile industry, there is a lot of wastewater and the composition of this wastewater is very pollutant, so it is considered the most polluting industry [2]. Pollution problems caused by textile industry wastewater have increased enormously in recent years. These wastewaters can cause a wide variety of environmental and toxicological effects.

Dyes used in the textile industry are potential hazards as they can turn into carcinogenic and toxic products. The direct release of textile wastewater into water bodies such as rivers is toxic to aquatic plants, microorganisms and fish. Textile dyes can cause various allergic reactions, skin irritation, irritation of the mucous membranes and upper respiratory tract [3].

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Azo dyes constitute the world's largest class of synthetic dyes. 60-70% of the dyestuffs produced in the world are azo dyes. Azo dyes can be reduced to aromatic amines by intestinal microflora and liver enzymes. These aromatic amines pose a threat to human health and ecosystems [4].

Textile wastewater must be physically and chemically treated before discharging into water bodies. The removal of dyes from wastewater by forces such as van der waals forces, electrical attraction, gravity is a physical treatment method [5.]. With these methods, the physical state of the substances can change, for example, dispersed substances can coagulate but the chemical change is not observed. Some of these methods are adsorption [6 -8], membrane filtration [9], and ion exchange [10]. Apart from physical methods, there are some chemical methods such as chemical precipitation [11], chemical oxidation [12], coagulation and flocculation [13]. Physical methods provide efficient removal of dyestuffs, but do not cause any degradation on dyestuffs. The dyestuffs removed from the aqueous solution cause a secondary pollution. The heterogeneous photocatalysis method using titanium dioxide as the photocatalyst is accepted as the method that causes the most degradation on dyes [14]. The use of titanium dioxide (TiO_2) as a catalyst for the removal of dyestuffs from water is advantageous because TiO_2 is readily available, inexpensive, strong and environmentally friendly. Therefore, decolorization of dyestuffs from aqueous solution using TiO_2 photocatalyst is highly preferred [15-19].

In this study, cross-linked polymer microbeads with photocatalytic properties were prepared by suspension polymerization method and used to remove azo dyes in an aqueous solution quickly, easily and without causing secondary pollution.

2. Material and Method

2.1. Chemicals

Acid violet 7 (dye content 40%) used as a dye in this study was obtained from Sigma-Aldrich (UK).

Crosslinker ethylene glycol dimethacrylate (EGDMA) was obtained from Merck (Darmstadt, Germany). benzoyl peroxide (BPO), used as the initiator, was obtained from Fluka (Switzerland). Stabilizer polyvinyl alcohol (PVAL; Mw: 100,000, 98% hydrolyzed) was obtained from Aldrich Chem. (USA). Monomer 2 Vinyl Pyridine (VP) was supplied by Merck (Darmstadt, Germany). TiO_2 (nanopowder) was obtained from Sigma-Aldrich (Germany). All other chemicals used in this study were reagent grade and were purchased from Merck AG (Darmstadt, Germany).

Table 1. Polymerization conditions of [poli(EGDMA-2-VP)]-TiO_2 polymer microbeads

Dispersion Phase	Organic Phase	Polymerization Conditions
50 mL Distilled water	5 mL EGDMA	Reactor Volume: 100 mL
0,2 g PVA	3 mL VP	Stirring Rate: 700 rpm
	10 mL Toluene	Time and temperature: 6 h, 60°C
	0,2 g BPO	
	0,5 g TiO_2	

2.2 Synthesis of the [poli(EGDMA-2-VP)]-TiO_2

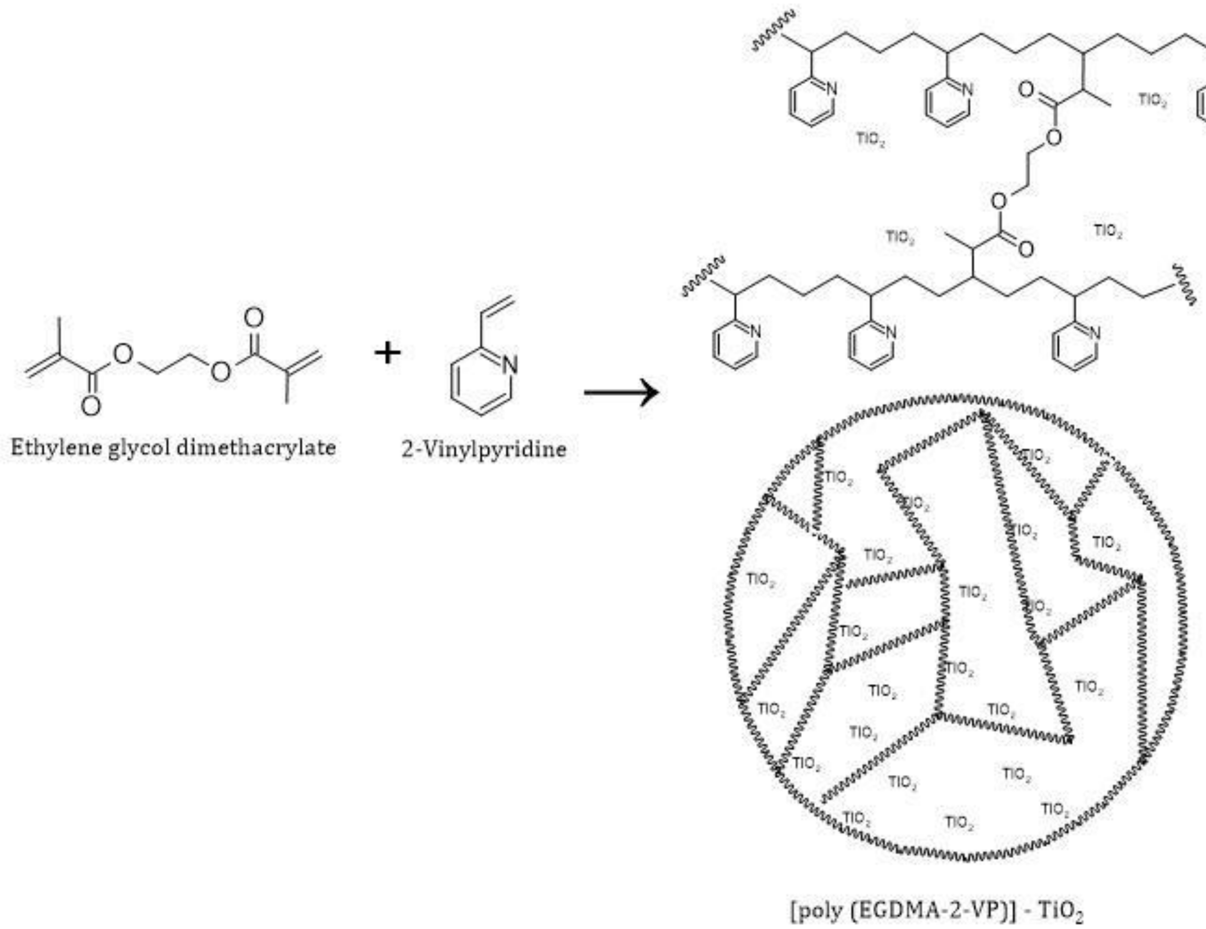
Polymer microbeads were synthesized by the suspension polymerization method. For the dispersion phase, 0.2 g of PVA was mixed in a magnetic stirrer until dissolved in 50 mL of distilled water. To prepare the organic phase, 0.2 g of benzoyl peroxide was added to 10 mL of toluene and dissolved. Then 5 mL of EGDMA and 3 mL of VP were added. The dispersion phase, 0.5 g of TiO_2, and the organic phase were added to the cylindrical polymerization reactor made of pyrex glass. The reaction occurred at a temperature of 60°C at a stirring speed of 700 rpm and for 6 hours. The polymer microbeads obtained at the end of the reaction were kept in a mixture of water and ethyl alcohol for 48 hours. The polymer microbeads were removed from the unreacted monomers and dried in a vacuum oven at 70°C for 48 hours.

2.3 Characterization studies

Surface photographs were taken by scanning electron microscopy (SEM) to determine the surface morphology of synthesized [poly (EGDMA-2-VP)] - TiO_2 microbeads. Fourier transform infrared spectrophotometer (FTIR) was used to analyze the chemical bonds in synthesized polymer microbeads. X-ray Diffraction (XRD) method was used to confirm the presence of TiO_2 in polymer microbeads.

2.4 Photocatalytic decolorization experiments

For photocatalytic decolorization of acid violet 7 dye from aqueous solution with [poly (EGDMA-2-VP)] - TiO2 microbeads, pH, dye concentration, polymer amount, time parameters were examined. All studies were carried out both with the CAMAG UV lamp 4 model device and under direct sunlight. The maximum absorption wavelength (λ_{max}) of the dye was determined as 526 nm by Uv-vis spectrophotometry. After the experiments, the dye concentration remaining in the aqueous phase was determined by a calibration graph. Percent removal after photocatalytic decolonization was calculated as;



Scheme 1. Polymerization scheme for the preparation of [poly (EGDMA-2-VP)] - TiO_2 microbeads.

$$\% \, Removal \, AV7 = \frac{Cin - Cfin}{Cin} x100 \qquad (1)$$

3.Results

3.1 Characterization

The surface morphology of [poly (EGDMA-2-VP)] - TiO_2 was elucidated by scanning electron microscopy. As seen in Figure 1, the polymers are in the form of microbeads and have a porous surface.

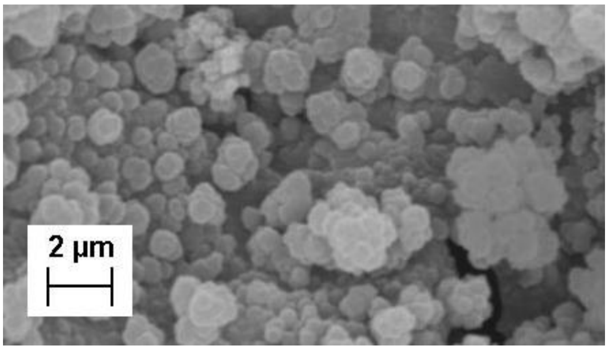


Figure 1. SEM image of [poly (EGDMA-2-VP)] - TiO_2

The structure of the bonds in the [poly (EGDMA-2-VP)] - TiO_2 microbeads was elucidated by FTIR and the FTIR spectrum is given in the Figure 2 (a). The peak at 1724 cm^{-1} is related to the C=O stretching of the ester functional group in the EGDMA structure. The peak at 2951 cm^{-1} belong to the C-H bond in methylene. The peak found at 1145 cm^{-1} belong to the C-O stretching. The peaks at 1670 cm^{-1} (C=N stretching), 1423 cm^{-1} (C=C stretching) and 1269 (C-N stretching) are related to the characteristic pyridine ring. The peak at 1462 cm^{-1} is related to Ti-O-Ti stretching of TiO_2.

The presence of TiO_2 in polymer microbeads was determined by XRD and the XRD pattern is given in the Figure 2 (b). The peaks at 24° and 48° indicate that TiO_2 in the polymer microbeads is in the anatase phase, which is known to have the best photocatalytic effect [20]. The graph is inclined because the polymer matrix is amorphous [21].

3.2 pH effect on decolorization

The effect of pH on the maximum decolorization of AV7 was investigated by keeping all other parameters constant. The change in % removal with pH is given in the Figure 3. TiO_2 surface is positively charged in acidic environment [22]. The interaction between AV7 and TiO_2 is best in an acidic environment. With the increase in pH, the amount of photocatalytically degraded dye decreased.

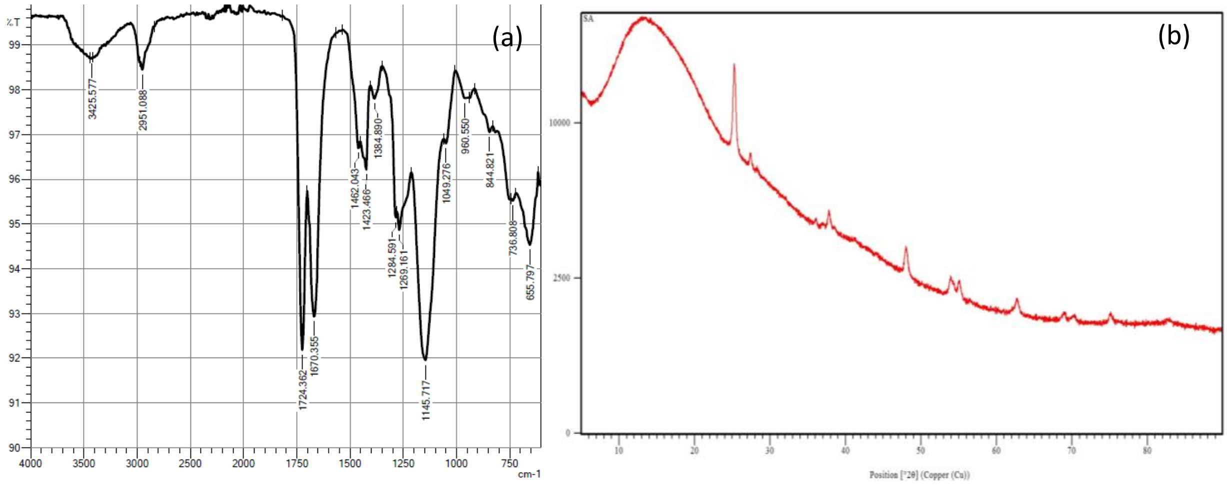


Figure 2. (a) FTIR spectrum of [poly (EGDMA-2-VP)] - TiO_2, (b) XRD patterns of [poly (EGDMA-2-VP)] - TiO_2

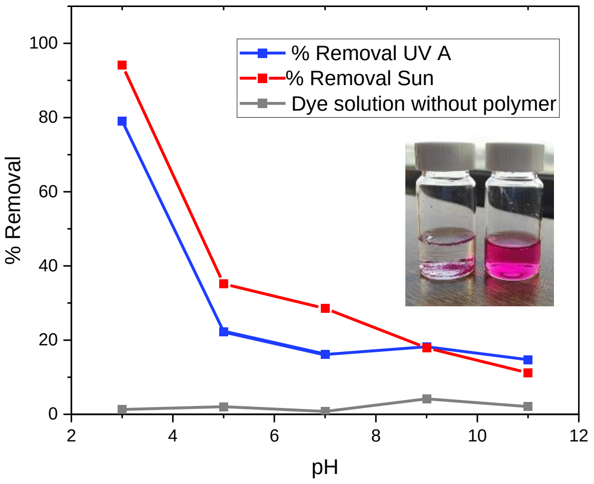


Figure 3. Photocatalytic decolorization effect of pH on AV7 dye

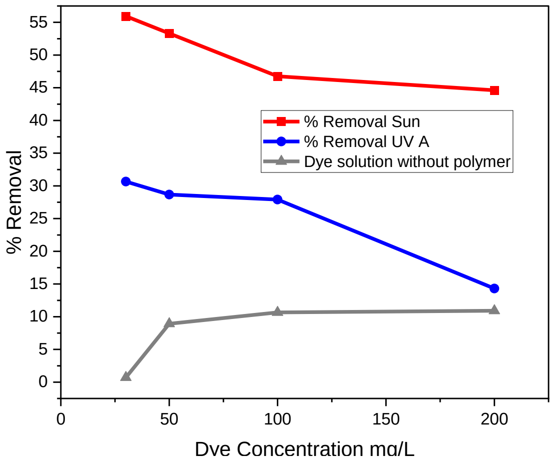


Figure 5. Effect of dye concentration on photocatalytic decolorization of AV7 dye.

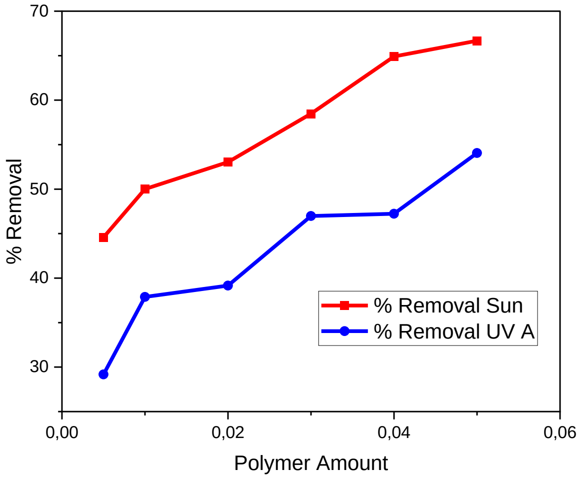


Figure 4. Effect of polymer amount on photocatalytic decolorization of AV7 dye

3.3 Effect of polymer amount on decolorization

The effect of polymer amount on decolorization was investigated by keeping all other variables constant. The relationship between % removal and polymer content is given in the Figure 4. Decolorization increased with the increase in the amount of polymer. The reason for this situation can be explained by the fact that the incoming photons encounter more surfaces and the formation of more radical groups [23].

3.4 Effect of dye concentration on decolorization

The effect of dye concentration on decolorization was investigated keeping all other parameters constant. The relationship between dye concentration and % removal is given in the Figure 5. According to Lambert-Beer law, the light reaching the catalyst decreased with increasing concentration. Therefore, % removal decreased with increasing concentration.

3.5 The effect of time on decolorization

To investigate the effect of time on decolorization, studies were carried out keeping all other parameters constant. Over time, the % removal has increased.
The characteristic absorbances of AV 7 dyestuff at 302 and 526 nm were measured using UV visible spectrophotometer depending on time. The absorbance at 526 nm refers to the color of the dye. The absorbance at 302 nm refers to the aromatic part in the structure of the AV7 dyestuff. The decrease in the absorbance peaks seen in Figure 7 with time indicates that the dye degraded over time and the solution becomes colorless [24].

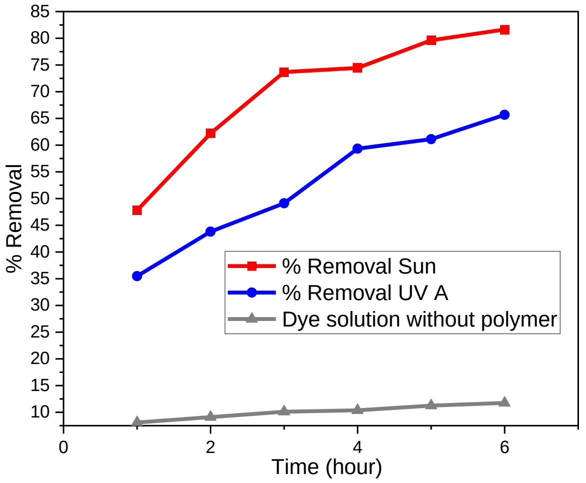


Figure 6. Effect of time on photocatalytic decolorization of AV7 dye

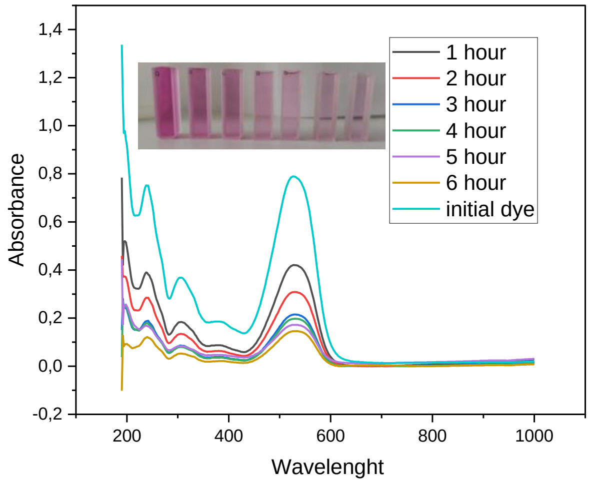


Figure 7. Degradation of AV7 changes in the UV-vis spectrum

3.6 Kinetic studies

The ln (C_0/C)-t plot was drawn to determine a suitable model for decolorization kinetics. As seen in the Figure 8, logarithmic C_0/C has given a linear graph with time. The reaction is amenable to first-order reaction kinetics.

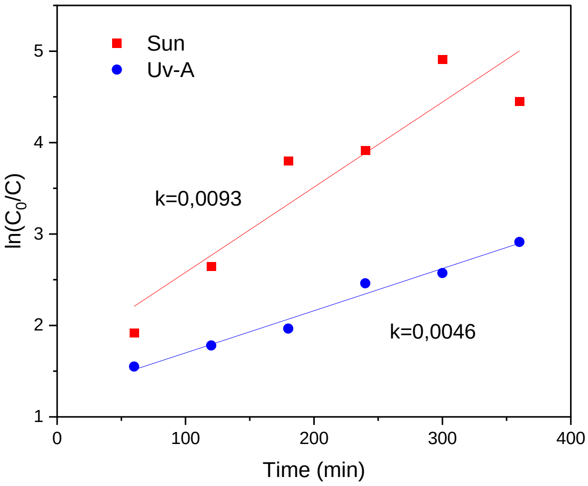


Figure 8. Photocatalytic decolorization kinetics of AV7

The reaction rate constant is obtained from the slopes of the lines. The rate constants are 0.0046 min^{-1} and 0.0093 min^{-1} under UVA light and sunlight, respectively. The increase in the rate constant indicates that the photocatalytic effects of the polymer microbeads are better under sunlight [25].

4. Conclusions

In this study [poly (EGDMA-2-VP)] - TiO2 cross-linked microbeads were synthesized and optimum conditions for photocatalytic dye removal were determined. The conditions under which the maximum photocatalytic decolorization of the dyestuff were pH 3, polymer amount 0.05 g, dye concentration 30 mg / L, and time 5 hours. It was determined that the reaction rate fit the first-order kinetic model. [poly (EGDMA-2-VP)] - TiO2 microbeads removed dyestuffs from aqueous solution faster than using TiO_2 nanopowder alone, and removed from aqueous solution by an easier filtering process than TiO_2 nanopowder. The results showed the usability of [poly (EGDMA-2-VP)] - TiO_2 microbeads for dye decolorization quickly, easily, without causing secondary pollution.

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Declaration of Ethical Code

In this study, we undertake that all the rules required to be followed within the scope of the "Higher Education Institutions Scientific Research and Publication Ethics Directive" are complied with, and that none of the actions stated under the heading "Actions Against Scientific Research and Publication Ethics" are not carried out.

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