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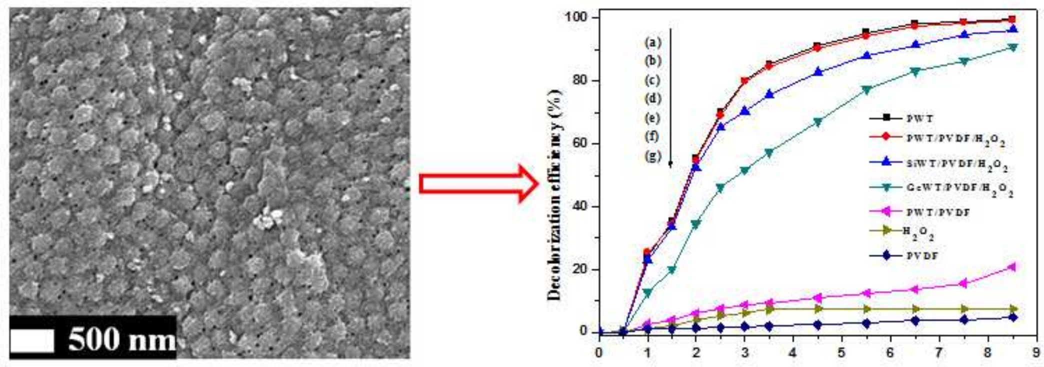
Graphical abstract:

A new composite membrane based on Keggin POMs and PVDF not only exhibits good photocatalytic activity and repeatability, but also can be easily handled and recycled.



A new composite membrane based on Keggin Polyoxotungstate/ Poly(vinylidene fluoride) and its Application in Photocatalysis

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Abstract: Polyoxometalate (POM) is a promising candidate as photocatalyst for the removal of organic pollutants from water, showing striking similarities to TiO_2. However, the drawback of high solubility in solution making it difficult recovering and recycling impedes its potential applications in wastewater treatment. We have developed a new composite membrane based on Keggin POM and poly(vinylidene fluoride) (PVDF) via combining doctor-blade method, immersion precipitation and colloid interface techniques. The as-prepared composite membrane was characterized by FTIR, SEM and X-ray EDS, revealing that the Keggin POM could be homogenously intermingled in the composite membrane. The composite membrane not only exhibits good degradability on methyl orange in the presence of H_2O_2 and excellent photocatalytic repeatability maintaining 97.36% decolorization efficiency of initial one even after 8 cycles, but also can be easily handled and recycled.

Keyword： Polyoxometalate; Poly(vinylidene fluoride); Keggin; Photocatalytic; Methyl orange

1. Introduction

With the rapid development of economy and society, serious environmental problems, such as the increasing contamination of water and air, have attracted more and more scientists' attention.[1, 2] To reduce the impact of environmental pollution, photocatalysts have been extensively studied as excellent materials for the elimination of hazardous organic compounds in contaminated water and air.

Polyoxometalate (POM), as a large variety of oxygen-bridged metal cluster with unique structural characteristics, has been a promising green and cheap photocatalyst for the removal of organic pollutants or transition metal ions from water.[2-9] POM as photocatalyst exhibits striking similarities to TiO_2 in terms of the overall mechanism of photodecomposition of organic compounds, the intermediate species and the final photodegradation products.[10-12] Ultraviolet light induces POM to produce oxygen-to-metal charge transfer (OMCT) with promoting electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).[13-17] The charge-transfer excited state (POM*) with oxidising property can direct oxidize the target pollutant, or react with water or other electron acceptor to generate •OH radical..[2, 11] But the drawback of high solubility in solution making them difficult recovering and recycling impedes their potential applications in wastewater treatment. Many researchers have made efforts in order to resolve this problem. Incorporation of homogeneous POM with supporting materials, such as TiO_2, Ta_2O_5, ZrO_2, and SiO_2, has been extensively investigated.[18-10] Although those hybrids overcome some difficulties in recovering and recycling, these methods have other shortcomings such as limited activity or stability during the reaction.[21] Conversely, the polymer membrane as support may have more advantages, such as high stability, low cost and much easier separation from reaction solution if the organic polymers can avoid of UV light degradation of themselves. Many studies have focused on the use of organic polymer as matrix support for photocatalytic material, especially in the preparation of heterogeneous catalysts. Some organic polymers with UV light resistance, such as poly tetrafluoroethylene,[22] cellulose microspheres,[23] polystyrene beads,[24] cationic exchange resin,[25] polyethylene oxide,[26] chitosan,[27] and poly(vinylidene fluoride) (PVDF)[28, 29] have been used as the support for photocatalysts. The TiO_2/poly(dimethylsiloxane) (PDMS) composite membrane directly coated on ploy(methyl methacrylate) (PMMA) substrates by a sol-gel method showed good photocatalytic activity.[30] The PDMS-W_{10}, Polyether Ether Ketone (PEEK)-W_{10} and PVDF-W_{10} polymer membranes as heterogeneous photocatalysts for the oxidation of a series of alcohols were also fabricated.[28] However, the composite membrane as photocatalyst based on Keggin POM and PVDF for decomposing organic dyes has not been reported yet.

In this paper, we will report a new composite membrane constructed from Keggin POM and PVDF by combining doctor-blade method, immersion precipitation and colloid interface techniques. The composite membrane not only exhibits good degradability on methyl orange in the presence of H_2O_2 under UV light irradiation and excellent photocatalytic repeatability, but also can be easily handled and recycled.

2. Materials and methods

2.1. Materials

Poly(vinylidene fluoride) (PVDF, with the trade name Kinar 460), N,N'-dimethylacetamide (DMA), 12-Tungstophosphoric acid ($H_3PW_{12}O_{40}$, PW),12-tungstosilicatic acid ($H_4SiW_{12}O_{40}$, SiW), and 12-tunstogermanic acid ($H_4GeW_{12}O_{40}$, GeW) were used in this work. Tetrabutylammonium Bromide ($C_{16}H_{36}NBr$, TBA), as a counter cation, was reacted with PW, SiW, GeW to get the lipophilic salt of dodecatungstate (PWT, SiWT, GeWT). Methyl orange (MO) was used as a photocatalytic degradation target. The above materials were all purchased from Shanghai Chemical Reagents Co., China and used without purification.

2.2. Preparation of PWT/PVDF Composite

PWT was prepared by the exchange of the counter cation:[31] A TBA aqueous solution (7.22×10^{-2} M, 5ml) was dropped into PW aqueous solution (8.02×10^{-3}M, 15ml), and the reaction mixture was then refluxed under a nitrogen atmosphere at 75 °C for at least 24 hours. Finally, the product was filtered and washed with ethanol, distilled water, and dried at 60 °C for 24 hours in vacuum (yield: 35%). The obtained

PWT can be dissolved in common organic solvents, such as DMA, ethanol, chloroform, etc.

The PWT/PVDF composite membrane was prepared as following: [32, 33] A suitable polymer PVDF(15.0 wt%) was dissolved in DMA(80.0 wt%) by magnetic stirring at room temperature, then the lipophilic salt of PWT (5.0 wt%) was added and was stirred in a closed flask at room temperature for at least 24 hours to form sol-gel solution. A plastic adhesive tape was fixed on the four sides of the cleaned glass sheet to restrict the thickness and area of the composite membrane. The colloid was spread on the glass sheet with a glass rod by a doctor-blade method. The membrane was immersed for 2 hours in coagulation bath containing deionized water at 25 ^{o}C, and then was separated and dried in a vacuum oven at 60 ^{o}C for 24 hours. Thus, the PWT/PVDF composite product was obtained. The similar way was also used to prepare the SiWT/PVDF and GeWT/PVDF composite membrane.

2.3. Photocatalytic experiments

Photocatalytic reaction was carried out in a Pyrex reactor of 250 ml capacity attached to an inner radiation type with 100W high-pressure mercury lamp as UV light source. The inner cell had thermostatted water flowing through a jacket between the mercury lamp and the reaction chamber, and the system was open to the air. The photocatalytic activities of samples were evaluated by measuring the degradation efficiency of methyl orange solution after a regular interval UV light irradiation, the steps were as follows: [34]

A single piece of composite membrane (size: 2.0×5.0 cm, weight: 0.2 g) was placed on the internal wall of the cell opposite to the light source to collect all the focused radiation. A 100 ml 15 mg/l methyl orange solution containing 1.5 mmol/l H_2O_2 (pH = 2.5) was placed in the cell under magnetic stirring. Prior to irradiation, the mixed suspension was allowed to stand for 30 min to reach absorption equilibrium due to the methyl orange concentration difference between the solution and inside of PWT/PVDF composite. After a fixed irradiation time, 3 ml solution was draw from the reaction chamber. The MO concentration (C) was determined by measuring the maximum absorbance at 505 nm as a function of irradiation time using a Lambda35 spectrophotometer (Perkin–Elmer, USA). The decolorization efficiency (D) of methyl orange solution was calculated by the following formula:

$$D = \frac{C_0 - C_1}{C_0} \times 100\% = \frac{A_0 - A_1}{A_0} \times 100\% \qquad (1)$$

where D is decolorization efficiency (%) , C_0, A_0 and C_1, A_1 are the concentration and absorbency of methyl orange solution at the peak of 505 nm before and after irradiation, respectively.

The reproducibility of the photocatalytic degradation activity on PWT/PVDF composite was studied at a 100 ml MO solution (15 mg/l, pH = 2.5) containing 1.5 mmol/l H_2O_2 and a catalyst dosage of 2 g/l (effective dosage: 0.5 g/l) in each cycle after two hour irradiation. At the end of irradiation, the composite membrane was separated from the reaction mixture, washed with water, exposed to oxygen atmosphere overnight and then was dried under vacuum. Before cycling, the weight of PWT/PVDF was measured by Mettler Toledo Balance (MS105DU). Then the recovered photocatalyst was reused in the next cycle. PWT concentration in the PWT/PVDF was analyzed by a Jobin Yvon Ultima2 ICP atomic emission Spectrometer before the 1st and after 8th cycle. For comparison, 0.2 g polymer PVDF membrane was placed in the concentrated POM solution (10 g/l) under two hour UV irradiation. After separated, washed and dried in vacuum, the weight of PVDF was also measured and used in the next cycle.

2.4. Characterizations

Elemental analyses (C, H, and N) for PWT, SiWT and GeWT were carried on an Elementar Vario EL III analyzer. W is determined by a Jobin Yvon Ultima2 ICP atomic emission Spectrometer. (1) For PWT: $(C_{16}H_{36}N)_3(PW_{12}O_{40})$ Anal. Calcd.: C, 16.00%; H, 3.02%; N, 1.17 %; W, 61.21%. Found for $(C_{16}H_{36}N)_{2.91}H_{0.09}(PW_{12}O_{40})$: C, 15.61%; H, 2.94%; N, 1.14 %; W, 61.56 %. (2) For SiWT: $(C_{16}H_{36}N)_4(SiW_{12}O_{40})$ Anal. Calcd.: C, 20.00%; H, 3.78%; N, 1.46%; W, 57.39%. Found for $(C_{16}H_{36}N)_{3.87}H_{0.13}(SiW_{12}O_{40})$: C, 19.51%; H, 3.69%; N, 1.42%; W, 57.86%. (3) For GeWT: $(C_{16}H_{36}N)_4(GeW_{12}O_{40})$ Anal. Calcd.: C, 19.77%; H, 3.73%; N, 1.44%; W, 56.74%. Found for $(C_{16}H_{36}N)_{3.88}H_{0.12}(GeW_{12}O_{40})$: C, 19.32%; H, 3.65%; N, 1.41 %; W, 57.17%.

Scanning electron microscope (SEM) micrographs and X-ray elemental analysis were performed by the field emission SEM (JSM-6700F). Fourier transform infrared (FTIR) spectra were recorded in the range 400–4000 cm^{-1} on a Perkin Elmer Spectrum using KBr pellets. The absorption spectra of the samples were measured by using a Lambda35 spectrophotometer (Perkins-Elmer, USA).

3. Results and Discussion

3.1. Morphology of the PWT/PVDF

Figure 1. Here

The SEM image of PWT/PVDF membrane with 25% of PWT is shown in Fig. 1a, and the corresponding X-ray emission map obtained using the X-ray energy dispersive spectrometry (EDS) detector is presented in Fig. 1c in which white points of tungsten can be observed. Fig. 1b shows the membrane with 30% of PWT. As seen from Fig. 1a and 1b, the surface morphology of the membrane with 25% of PWT is much evener than that of the membrane with 30%. Besides, there are some holes and present agglomerates as observed in Fig. 1b. The phenomenon demonstrates that suitable PWT can be well dispersed into the polymer PVDF. The image of Fig. 1c exhibits a uniform dispersion of tungsten, indicating that the PWT was intermingled homogenously in the polymer PVDF. Thus, we selected PWT/PVDF of 25% PWT to examine the photocatalytic experiments.

3.2. FTIR Spectra

Figure 2. Here

As shown in PWT spectrum (Fig. 2a), the absorption peaks at 1081, 1043, 955, 904, 508 cm^{-1} are fundamentals for $PW_{12}O_{40}^{3-}$, which indicate that the Keggin units were not destroyed during the ion-exchange. Fig. 2b exhibits the FTIR spectrum of the PWT/PVDF composite membrane. In the spectra of the PWT/PVDF composite samples, the characteristic bands of POM appear slight shift, indicating that PWT and PVDF have interaction with each other and the structure of $PW_{12}O_{40}^{3-}$ is still preserved inside the PWT/PVDF composite. It is concluded that the POM structure remains stable after immobilizing in PVDF matrix. Fig. 2c is the FTIR spectrum of the PWT/PVDF composite after 8th cycles of photocatalytic reaction. Its absorption bands are very similar to those of Fig. 2b, confirming that the original framework of $PW_{12}O_{40}^{3-}$ was not destroyed after several cycles of photocatalytic reactions in the composite membrane.

3.3. Photocatalytic property

Figure 3. Here

The variations in the decolorization efficiencies of MO solution under various conditions are shown in Fig. 3. Curve A in Fig. 3 is the initial time (0.5 hour for all samples) during which the whole system was stirred in the dark, and curve B (from 0.5 hour to 8.5 hours) denotes the time for the mixture to be exposed to UV light irradiation. In the dark, there is negligible degradation of MO solution even in the presence of catalyst and H_2O_2. Only after the UV light irradiation started, the degradation of MO was initiated. After 8.5 hours, the decolorization efficiency of MO solution can achieve 98.35% (curve b). Limited photodegradation of the MO in the absence of H_2O_2 system (curve e) were observed, indicating that H_2O_2 is an efficient electron acceptor in the heterogeneous PWT/PVDF system. Meanwhile the decolorization efficiency at the presence of only H_2O_2 (curve f) was very low, implying that PWT/PVDF is an effective photocatalyst. To understand the role of PWT and PVDF in the composite, we also compared the decolorization efficiencies of the PWT, PVDF, and PWT/PVDF. As shown in Fig. 3a and 3g, the decolorization efficiency of PWT is a little higher than that of PWT/PVDF under the same effective catalyst dosage, indicating that the support PVDF doesn’t hinder catalytic reaction activity. While the decolorization efficiency of polymer PVDF is almost zero, showing that the support PVDF has no photocatalytic activity under UV irradiation. On the other hand, the central atom in the Keggin unit of POM has a significant effect on the properties. We compared the photocatalytic activities of three composite membranes of different POM under the same conditions. The results are also presented in Fig. 3c and 3d. It is obvious that the photocatalytic activities among the Keggin unit of POM for MO follows the order of PWT/PVDF>SiWT/PVDF>GeWT/PVDF, which is consistent with the reactivity order in other photocatalytic reactions.[36, 37]

3.4. Photocatalytic kinetic

Figure 4. Here

PWT/PVDF composite membrane was selected as photocatalyst to investigate the kinetic of MO degradation in aqueous solution, and the results are depicted in Fig. 4. It follows an apparent first-order in good agreement with a generally observed Langmuir-Hinshelwood kinetics model: [26]

$$r = \frac{-dC}{dt} = \frac{kKC}{1+KC} \qquad (2)$$

where r is the degradation efficiency of the reactant (mg/l h), C is the concentration of the reactant (mg/l), t is the illumination time (h), k is the kinetic constant (mg/l h), and K is the adsorption coefficient of the reactant (l/mg). When the initial concentration C_0 is micromolar solution, the Equation (2) can be simplified to an apparent first-order equation:

$$In\left(\frac{A_0}{A}\right) = In\left(\frac{C_0}{C}\right) = kKt = k_{app}t \qquad (3)$$

The plot of $In(A_0/A)$ versus time represents a straight line, the slope of which upon linear regression gives rate constant K_{app} (0.607 h^{-1}).

3.5. Effect of H_2O_2

Figure 5. Here

Fig. 5 shows the initial decolorization efficiency of methyl orange (15 mg/l, pH = 2.5) containing different H_2O_2 concentration after two hour irradiation. The decolorization efficiency increases with increase of H_2O_2 concentration from 0.4 to 1.5 mmol/l, and then decreases with increase of H_2O_2 concentration from 1.5 mmol/l to 2.0 mmol/l. The optimum concentration of adding H_2O_2 is about 1.5 mmol/l. In photocatalytic degradation process, addition of adequate H_2O_2 is beneficial to the formation of hydroxyl radicals.[39, 40] H_2O_2 will facilitate the generation of ·OH and promote the decolorization efficiency. However, under the condition of exorbitant H_2O_2 concentration, H_2O_2 acts as a scavenger of ·OH and exhaust ·OH in solution, and the decolorization reaction will be retarded, therefore, only moderate added H_2O_2 is beneficial to achieve higher degradation efficiency. [39, 40]

3.6. Proposed mechanism

It is well known that POM can decompose a variety of organic pollutants via the formation of the common powerful oxidizing reagent from the reaction of the excited state or water or other electron acceptors, being very similar to TiO_2.[10-12] In this work, the polymer PVDF support makes the catalyst easier to be recycled and reused, and has no contribution to the photocatalytic activities. Meanwhile, the added H_2O_2 plays an important role in the photodegradation process. Thus, the photocatalytic mechanism of the PWT/PVDF composite membrane may be depicted as following: [2]

$$\text{PVDF-in-}POM \xrightarrow{h\nu} \text{PVDF-in-}POM^{*} \qquad (4)$$

$$\text{PVDF-in-}POM^{*} + H_2O \longrightarrow \text{PVDF-in-}POM^{-} + H^{+} + {}^{\bullet}OH \qquad (5)$$

$$\text{PVDF-in-}POM^{-} + O_2 \longrightarrow \text{PVDF-in-}POM + {}^{\bullet}O_2^{-} \qquad (6)$$

$$H_2O_2 + {}^{\bullet}O_2^{-} \longrightarrow O_2 + OH^{-} + {}^{\bullet}OH \qquad (7)$$

$$H_2O_2 \xrightarrow{h\nu} 2{}^{\bullet}OH \qquad (8)$$

$${}^{\bullet}OH + \text{MO (dye)} \longrightarrow \text{degradation product} \qquad (9)$$

UV excitation of POM induces oxygen-to-metal charge transfer (equ. 4), and the charge-transferred excited state POM^* has a highly oxidizing power that is strong enough to oxidize H_2O to generate hydroxyl radicals (equ. 5).[2] The POM core is like a *reservoir* of electrons which can undergo electron reduction processes.[4] In the presence of dioxygen, the reduced catalyst (PVDF-in-POM^{-}) undergoes an easy reoxidation to parent one through the transfer of electron from reduced species to dioxygen (equ. 6), keeping the photocatalytic cycle persisting. H_2O_2 will facilitate the generation of ${}^{\bullet}OH$ and promote the photodegradation efficiency (equ. 7 and 8). Then, the radicals attack organic substrates and degrade dye (equ. 9).

3.7. Reproducibility of photocatalyst

Figure 6. Here

The reproducibility of the photocatalytic activity for the photocatalyst is a very important parameter to assess the photocatalyst practicability.[39] Fig. 6 exhibits the decolorization efficiency of MO by PWT/PVDF composite membrane in different recycling times. It is observed that the decolorization efficiency decreases from 69.05%

to 67.23% after eight cycles for PWT/PVDF membranes, which maintains 97.36% of initial decolorization efficiency, indicating that the photocatalytic activity has a better repeatability. For further investigating the reason about the little decrease of decolorization efficiency with the increase of recycling times. The weight of PWT/PVDF before and after photocatalytic degradation reaction was measured (Table S1), and PWT concentration in the PWT/PVDF was analyzed before the 1st and after 8th cycle (Table S1). For comparison, the weight of PVDF photodecomposed by PWT was also measured (Table S2). As seen from Table S1 and S2, the weight of PWT/PVDF, the PWT concentration in PWT/PVDF and the weight of PVDF all have a little decrease with the increase of recycling times. Thus, it can be deduced that the reason about the very little decrease of decolorization efficiency with the increase of recycling times may be the degradation of PVDF and the losing of POM. In conclusion, the PWT/PVDF composite membrane exhibits a simple recycled procedure and a better reproducibility of photocatalytic degradation, which is of great significance for practical use of the POM photocatalyst.

4. Summary

We have successfully developed a PWT/PVDF composite membrane by combining the doctor-blade method, immersion precipitation and colloid interface techniques. The PWT/PVDF composite membrane exhibits good UV light photocatalytic activity to decompose MO solution and excellent photocatalytic repeatability. Moreover, the composite membrane can be easily handled and recycled, thus indicating great practicability. This study also shows that the water-soluble POM can be immobilized into a polymer matrix, which may provide a new way to prepare an insoluble and readily separable solid for photocatalytic degradation of organic pollutants in the solution.

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FIGURE CAPTIONS.

Figure 1. SEM image of PWT/PVDF composite with 25% PWT (a) and the corresponding X-ray emission dot map (c) obtained with an X-ray fluorescence microprobe showing tungsten as white points, and SEM image of PWT/PVDF with 30% PWT (b).

Figure 2. Infrared spectra of PWT/TBA (a), PWT/PVDF composite (b) and PWT/PVDF after photodegradation reaction (c).

Figure 3. Photocatalytic decolorization efficiency for methyl orange (MO) with different POM/PVDF composite membranes. MO concentration: 15mg/l; pH: 2.5; POM/PVDF dosage: 2 g/l (effective dosage, 0.5 g/l) ; PWT, 0.5 g/l. (a) PWT; (b) PWT/PVDF/H_2O_2; (c) SiWT/PVDF/H_2O_2; (d) GeWT/PVDF/H_2O_2; (e) PWT/PVDF: (f) H_2O_2; (g) PVDF.

Figure 4. First-order linear In(A_0/A) =f (t). MO concentration: 15mg/l; pH: 2.5; PWT/PVDF dosage: 2 g/l (PWT, 0.5 g/l); H_2O_2, 1.5 mmol/l .

Figure 5. Effect of H_2O_2 on the decolorization efficiency of methyl orange (MO) solution with PWT/PVDF composite. MO concentration: 15 mg/l; pH: 2.5; Dosage: 2 g/l (PWT, 0.5 g/l); irradiation time: 2 hours.

Figure 6. Photocatalytic decolorization efficiency for methyl orange with PWT/PVDF composite in different recycling times. MO concentration: 15 mg/l; pH: 2.5; Dosage: 2 g/l (PWT, 0.5 g/l); irradiation time: 2 hours.

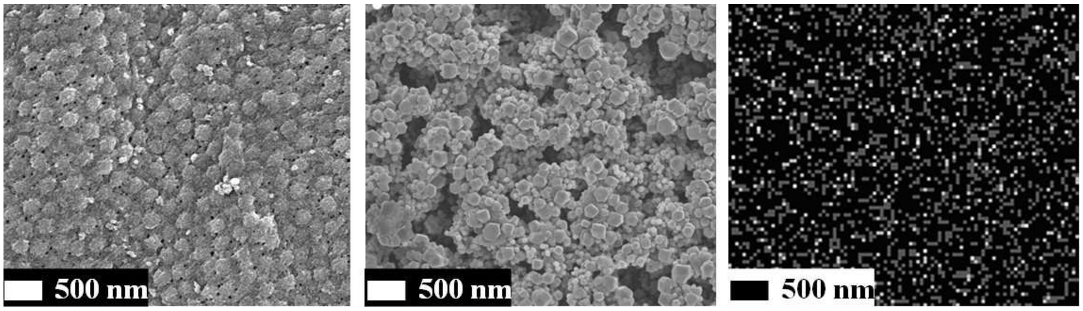

Figure 1.

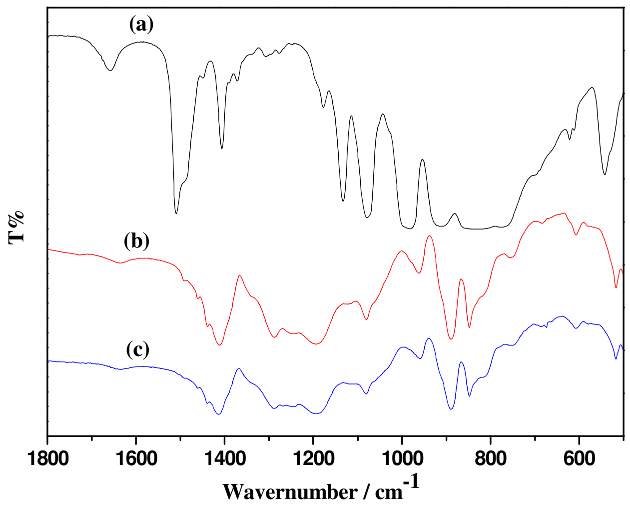

Figure 2.

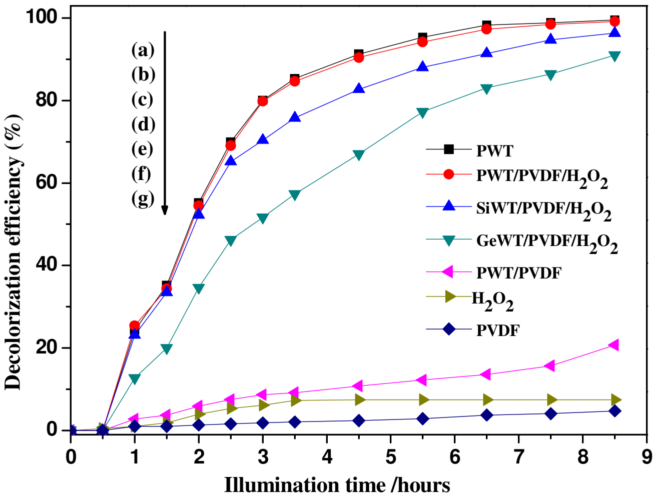
100
80
60
40
20
0
Decolorization efficiency (%)
0
1
2
3
4
5
6
7
8
9
Illumination time /hours
(a)
(b)
(c)
(d)
(e)
(f)
(g)
PWT
PWT/PVDF/H2O2
SiWT/PVDF/H2O2
GeWT/PVDF/H2O2
PWT/PVDF
H2O2
PVDF

Figure 3.

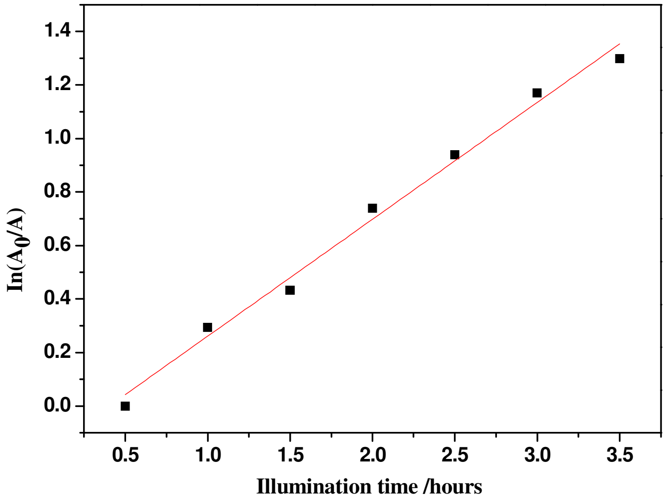
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
In(A_0/A)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Illumination time /hours

Figure 4.

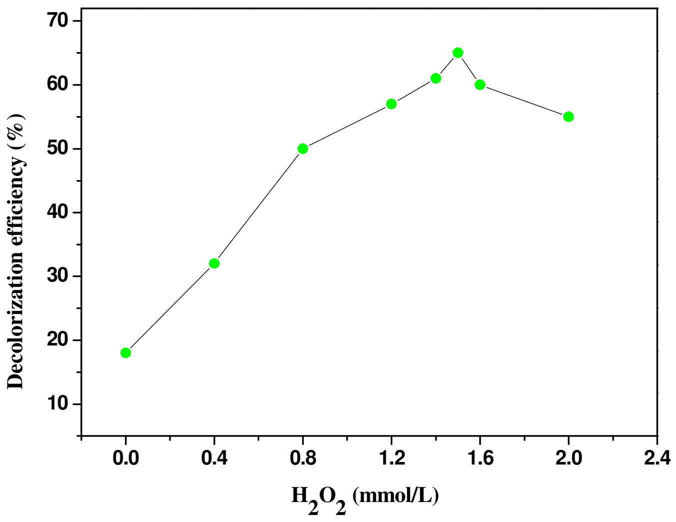
70
60
50
40
30
20
10
Decolorization efficiency (%)
0.0
0.4
0.8
1.2
1.6
2.0
2.4
H_2O_2 (mmol/L)

Figure 5.

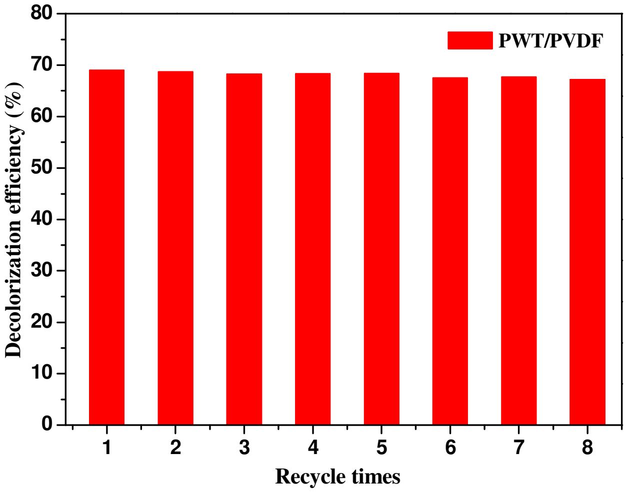
80
70
60
50
40
30
20
10
0
Decolorization efficiency (%)
1
2
3
4
5
6
7
8
Recycle times
PWT/PVDF

Figure 6.