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Synthesis of Ag-TiO₂/perlite composite for the photodegradation of methylene blue under solar light irradiation

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ABSTRACT

In this research, photocatalytic materials of TiO_2, Ag-TiO_2, Ag-TiO_2/perlite were synthesized by the sol-gel method. By combining the photocatalytic activity between Ag-TiO_2 and Perlite mineral, the Ag-TiO_2/perlite composite has overcome the disadvantages of pristine TiO_2, such as high band gap energy, low light utilization and easy recombination of electrons and holes. The synthesized samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), nitrogen adsorption-desorption isotherm, UV-vis diffuse reflectance spectroscopy (UV-vis DRS). The photocatalytic activity of the samples was tested for degradation of methylene blue (MB) under solar light irradiation. Photodegradation studies revealed a 95% removal of MB dye via the synthesized Ag-TiO2/perlite after 150 min of irradiation. Reusability of this hybrid photocatalyst system was tested and only a 3% decrease was observed after four cycles.

Introduction

In the field of photocatalytic environmental treatment, TiO_2 nanomaterials have received lots of attention from scientists [1, 2]. However, TiO_2 has a high band gap energy that requires ultraviolet irradiation to excite the electron-hole pairs to enhance the photocatalyst. Furthermore, the rapid recombination of the photochemical electron-hole pairs can significantly reduce the catalyst's efficiency. Therefore, narrowing the band gap energy of TiO_2 to increase its visible light absorption is a commonly used method to improve the photocatalytic efficiency. Several methods were used to narrow the band gap energy, such as adding metals or metal oxides of various elements to the lattice of TiO_2 like Zn, Fe, Cr, Eu, Y, Ag, Ni,...[3-7], adding non-metals like N, C, S, F, Cl,...[8-11] or simultaneously putting the mixture of elements into the lattice of TiO_2. Most of the modified products have a higher photocatalytic activity than pure TiO_2 in the visible light region. *G. Sanzone* et al. [12] synthesized Ag/TiO_2 membrane operating in the visible light region, with the surface plasmon resonance of Ag nanoparticles narrowing the band gap energy of the membrane material, thereby increasing photosynthesis efficiency. *Zhang* et al. [13] synthesized modified TiO_2 nanoparticles in polyamide (PNP) lattice doped by Ag nanoparticles by hydrothermal sol-gel method. Ag@TiO_2-0.5 was synthesized and removed 79.49 % methyl orange (MO) after 3 h of UV radiation, and it showed a faster reaction rate, about 2.7 times than pure TiO_2 nanoparticles. Thus, it can be said that doping Ag nanoparticles into the lattice structure of TiO_2 increases the absorption of visible light, reduces the

recombination of the e^-/h^+ pairs, thereby increasing photocatalytic efficiency.

Perlite is a rhyolitic glass made up of more than 70% silica and 13% alumina by weight [14]. Initially, perlite has a high density of approximately 1100 kg.m^3 (1.1 g/cm^3), while expanded perlite has a density of 30-150 kg.m^3 (0.03-0.05 g/cm^3). Using perlite as a carrier for synthesizing the photocatalyst of modified TiO$_2$ is a new approach to overcome disadvantages and improve photocatalytic efficiency. Perlite is a low-cost mineral resource available in nature; therefore, it is possible to make use of it. TiO$_2$/perlite composite materials have been synthesized through various methods. *Shavisi* et al. [15] studied the application of TiO$_2$/perlite photocatalyst to degradation of ammonia in wastewater. The efficiency of ammonia degradation using TiO$_2$/perlite photocatalyst reached 68 % after 180 minutes of solar light irradiation with optimal reaction conditions. *Giannouri* et al. [16] studied to synthesis TiO$_2$/Perlite composites by the one-step flame spray pyrolysis and their photocatalytic behavior through the oxidation of air pollutants.

This study aimed to investigate the photocatalytic activity of enhanced TiO$_2$, Ag-TiO$_2$ as photocatalysts. TiO$_2$, Ag-TiO$_2$ were immobilized on perlite granules to degrade MB from synthetic wastewater under solar light irradiation. The photocatalytic mechanisms induced by solar light-responsive Ag-TiO$_2$/perlite composite was also proposed to demonstrate the photodegradation of MB cationic dye.

Experimental

Materials

Raw perlite from Phu Yen province of Vietnam. The perlite consisted of SiO$_2$ 68.51 wt.%, TiO$_2$ 0.35 wt.%, Al$_2$O$_3$ 14.54 wt.%, FeO 3.52 wt.%, MnO 0.09 wt.%, MgO 1.04 wt.%, CaO 2.71 wt.%, Na$_2$O 3.6 wt.%, K$_2$O 4.29 wt.%, P$_2$O$_5$ 0.07 wt.% and others (LOI: 0.69 %). Ethanol (C$_2$H$_5$OH, 99,7 %), hydrogen peroxide (H$_2$O$_2$, 30%), titanium (IV) isopropoxide (Ti(OC$_3$H$_7$)$_4$, 99%), silver nitrate (AgNO$_3$, 99%), acetic acid (CH$_3$COOH, 99 %). All used chemical materials were purchased from Merk Co. All experiments were carried out by de-ionized water produced in the laboratory.

Ag-TiO$_2$/perlite photocatalyst synthesis process

Perlite purification process

20 g of raw perlite dissolved in 2000 mL of distilled water, stir continuously for 24 h, using a stirring paddle. Then let the mixture settle for 24 h, decant the middle part of the mixture to obtain pure perlite. Filtered, then dried at 120 °C and calcinated at 900 °C in 3 h to obtain pure expanded Perlite.

Synthesis of TiO$_2$ and Ag-TiO$_2$ nanoparticles

6 mL of acetic acid was put in a 50 mL glass beaker, cooled outside with ice, then quickly added 6 mL of Ti(OC$_3$H$_7$)$_4$ and sealed the beaker. The mixture is stirred for about 30 mins until the solution became transparent. Continue to add 12 mL of ethanol and shake to obtain sol-gel TiO$_2$. The sample was dried at 80 °C in 24 h and calcinated at 450 °C in 5 h with a heating rate of 5 °C/ min to obtain TiO$_2$.

An Ag-TiO$_2$ precursor solution was synthesized using sol-gel method. 3 mL of 0.3 M AgNO$_3$ was dissolved with 12 mL of ethanol in acidic conditions at room temperature, before being added to a mixed solution of the TiO$_2$ sol-gel. After stirring the mixed gel at 80 °C for 30 min. To obtain the Ag-TiO$_2$ photocatalyst powder, the gel was dried and calcined at 450 °C for 5 h with a heating rate of 5 °C / min.

Synthesis of Ag-TiO$_2$/perlite composite

1 g of Ag-TiO$_2$ was added to 60 mL of distilled water, stirring for 30 mins then ultrasonicated for 1 h (obtained solution A). 30 mL of C$_2$H$_5$OH and 3 g of perlite were stirred for 1 h and then added to solution A and continue stirring for 30 mins, then ultrasonicated for another 30 mins to obtain solution B. After that, solution B was put in an autoclave and placed in the oven at 180 °C in 4 h. The sample was filtered, washed, and dried at 80 °C to obtain Ag-TiO2/perlite composite finally.

Characterization

X-ray diffraction (XRD) of the samples was determined by using the diffractometer Bruker D8 Advance with Cu X-ray tube with wavelength λ(CuK$_\alpha$) = 1.540 Å. The accelerating voltage and applied current were 30 kV and 0.01 A, correspondingly. Surface morphology was observed by scanning electron microscopy (S-4800, Hitachi). Specific surface area Brunauer–Emmett–Teller was determined at N$_2$ temperature (77 K) by the N$_2$ desorption technique on the ChemBET-3030 system. Ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) of the sample at solid-state was recorded on spectrophotometer UV-2600 (Shimadzu).

Photocatalytic activity

The catalytic activity of the samples was evaluated through the photodegradation of methylene blue (MB) dye solution. Specifically, 50 mg of catalyst was added into a 50 mL glass beaker containing 35 mL of 50 mg/L MB solution. The mixture was stirred in the dark for 30 mins to reach the adsorption-desorption equilibrium. Then, the catalytic mixture was irradiated with solar light irradiation in 150 min. The concentration of MB in the solution at different times was analyzed by UV-Vis spectroscopy on UV 750 at a wavenumber of 664 nm.

Results and Discussion

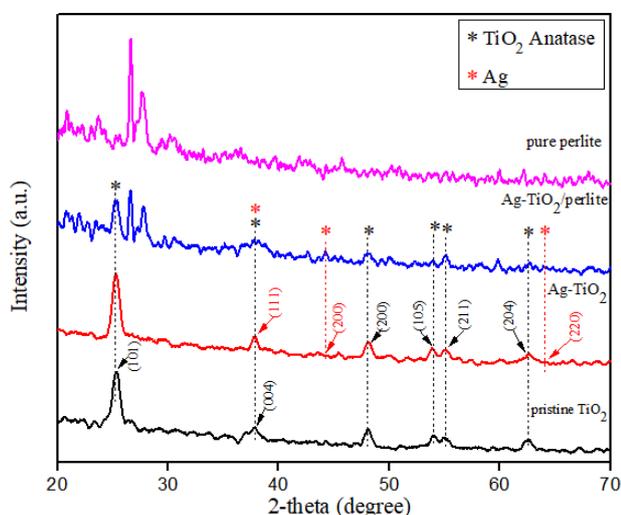XRD patterns of the synthesized photocatalytic samples are shown in Figure 1.

Figure 1: XRD patterns of pure perlite, TiO_2, Ag-TiO_2 and Ag-TiO_2/Perlite.

Figure 1 shows that the XRD patterns of TiO_2 anatase phase appeared at 2θ angles of 25.3°; 37.9°; 48.05°; 53.9° and 62.71° corresponds to an interlayer distance of (101); (004); (200); (105); (211) and (204). This is consistent with the JCPD 21-1271 standard spectrum of TiO_2 anatase phase. Diffraction peaks showed up clearly and sharp, with no other doped peaks, showing that the anatase phase structure of TiO_2 was well-formed during the synthesis process. Diffraction peaks at 2θ = 44.2° and 64.4° corresponding to the interlayer distance of (200) and (220), respectively, characteristic of Ag nanoparticles is consistent with JCPDS 65-2871 standard spectrum. On the other hand, reflector (004) at 37.9° angle of TiO_2 anatase corresponded with the characteristic peak (111) of Ag. The X-ray diffraction pattern of Ag-TiO_2/perlite sample showed that the characteristic diffraction peaks of Ag and TiO_2 were observed. In addition, characteristic peaks of pure perlite appeared at 2θ = 27° and 28.1°. Using Scherrer's equation, the estimated size of Ag nanoparticles corresponding to the facet (200) was about 19.59 nm and TiO_2 nanoparticles size corresponding to the facet (101) was approximately 12.05 nm.

The morphological surface of pure perlite and Ag-TiO_2/perlite was investigated using SEM images (Figure 2).
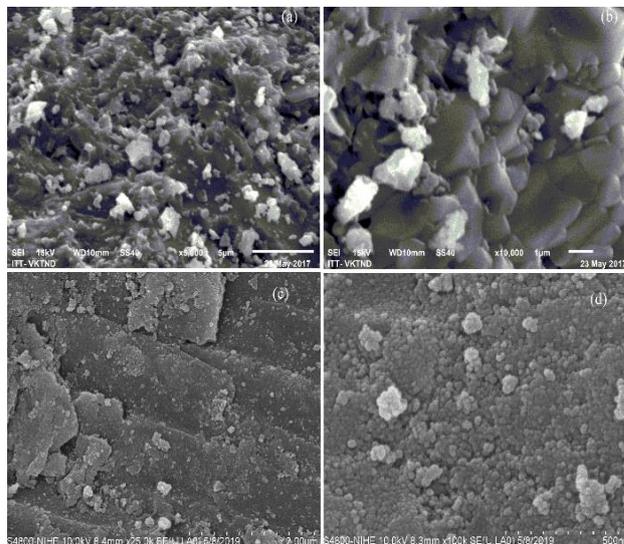

Figure 2: SEM images of perlite (a,b) and Ag-TiO_2/perlite composite (c,d).

SEM images of the perlite samples (Figure 2 a,b) showed that the expanded perlite has a highly porous structure, rough surface due to water loss when calcinated at high temperature to create small pores. In Figure 2 (c,d), Ag-TiO_2 nanoparticles covered the surface of perlite granules. The size of TiO_2 and Ag particles is approximately 30-40 nm, matched with the size calculation results by the X-ray diffraction method. Thus, Ag-TiO_2 was well-dispersed on the perlite carrier surface, and active phases of Ag-TiO_2 remained stable.

The surface area and pore size of the material were determined by the N_2 adsorption-desorption method (Figure 3).
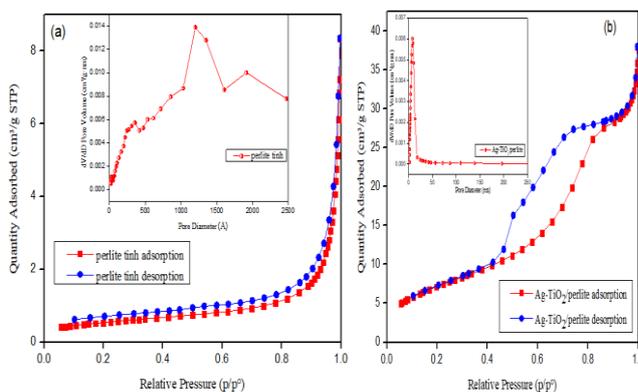
Figure 3: (a) N_2 adsorption-desorption isotherms and (b) pore size distribution of pure Perlite and Ag-TiO_2/perlite

The results indicate that the pure perlite has a surface area of 1.9 m^2/g and pore diameters of 26.4 nm. It was observed that after incorporating perlite into the Ag-TiO_2, the specific surface area of Ag-TiO_2/perlite composite increased dramatically, from 1.9 m^2/g for perlite to 26.66 m^2/g for the synthesized composite.

Distinct absorption in the visible region has a vital role for the visible-light and solar light energized catalyst. The photocatalytic properties of samples were studied by the diffuse reflectance spectroscopy UV-Vis DRS and the UV-vis absorption data for the TiO_2, Ag-TiO_2 and Ag-TiO_2/perlite are given in Figure 4.
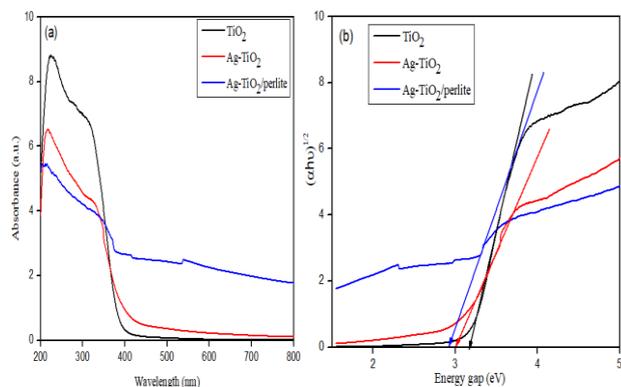

Figure 4: (a) UV-vis diffuse reflectance spectrum, (b) Kubelka-Munk equation of TiO_2, Ag-TiO_2, and Ag-TiO_2/perlite

The absorption edge of TiO_2 shifted to the greater wavelength region, from 406 nm to 441 nm, when Ag was doped onto the perlite support. The band gap energies of the samples were also estimated using Kubelka-Munk's equation [17]. TiO_2, Ag-TiO_2, Ag-TiO_2/perlite samples have band gap energies of 3.15; 3.0 and 2.9 eV, respectively. Thus, the presence of Ag nanoparticles contributed to the change of light absorption, led to the narrowing band gap energies of Ag-TiO_2 and Ag-TiO_2/perlite composite.

The photocatalytic activity of the samples was evaluated by MB degradation under solar light irradiation. The results are shown in Figure 5.

From Figure 5, when comparing TiO_2 and Ag-TiO_2, the MB degradation efficiency of Ag-TiO_2/perlite after 150 min under solar light irradiation was 95.54%, while the degradation efficiency after 150 min of TiO_2 and Ag-TiO_2 respectively were 71% and 80%. This can be due to the Ag-TiO_2/perlite photocatalyst has better activity under the visible light region, resulting in exciting new

photochemical electron-pairs. On the other hand, with surface structural advantage and porous system, MB degradation efficiency under solar light was highly efficient.
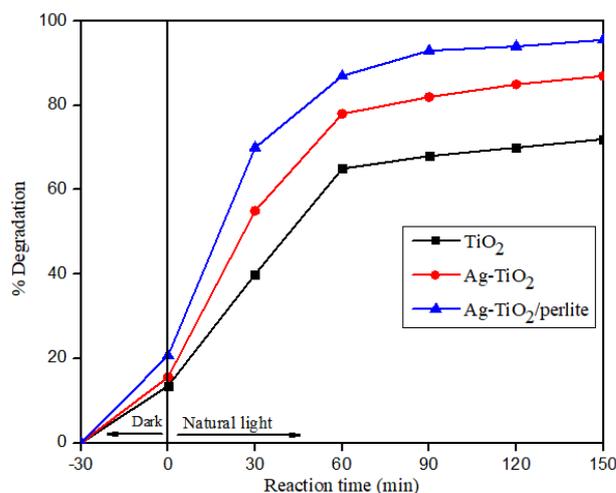

Figure 5: The effect of the various photocatalyst on the degradation of MB dye under solar light.
Reaction conditions: solar light irradiation (=750 lx), environment temperature (30 °C), pH=6.5

Many studies have pointed out the dependence of photocatalytic degradation rate on the amount of used catalyst. The effect of Ag-TiO_2/perlite catalyst dosage on MB photodegradation is shown in Figure 6.
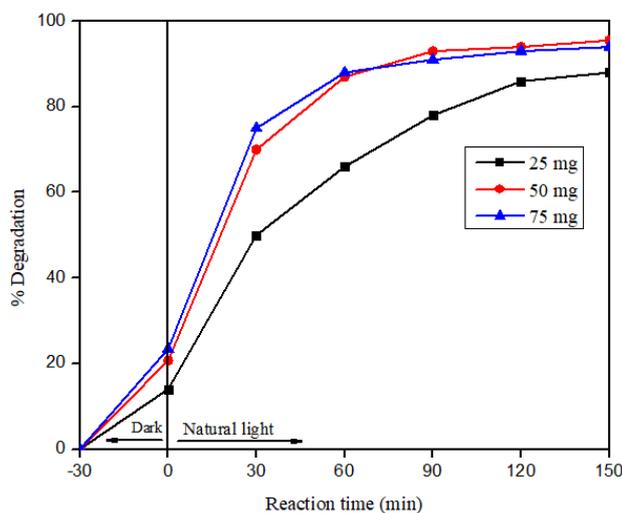

Figure 6: The effect of dosage catalyst Ag-TiO_2/perlite on photodegradation of MB dye under solar light.
Reaction conditions: solar light irradiation (=750 lx), environment temperature (30 °C), pH = 6.5

Using 50 mg of catalyst resulted in a maximum photocatalytic efficiency at 95% after 150 min and then decreased when the catalyst increased to 75 mg. With a high dosage of catalyst, the formation of active sites

will increase. However, when the amount of catalyst is too high, the interaction between surface layers of material reduces the formation of within photochemical electron-pairs and thus reduces the photocatalytic efficiency [18].

The concentration of oxidizing agent H_2O_2 also contributes to the MB dye decomposability of Ag-TiO_2/perlite composite (Figure 7).
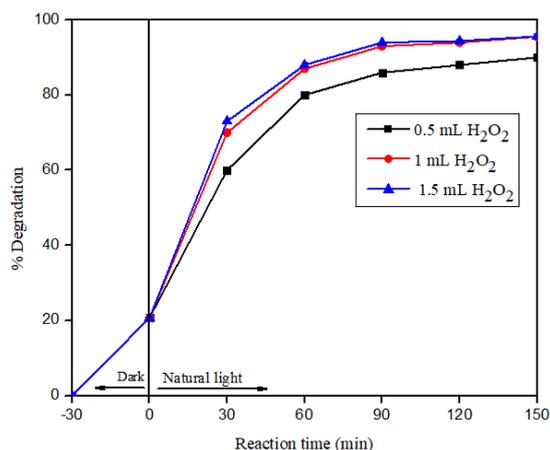

Figure 7: The effect of oxidizing agent (H_2O_2) on the degradation of MB dye under solar light.
Reaction conditions: solar light irradiation (=750 lx), environment temperature (30 ^oC), pH=6.5

MB dye degradation efficiency of the composite sample increases when increasing the oxidizing agent content. However, only a sufficient amount H_2O_2 should be used. Specifically, degradation efficiency increased from 90 % with the sample using 0.5 mL of H_2O_2 to 95.4 % with 1.0 mL of H_2O_2 and remained stable at 95.6 % when using 1.5 mL H_2O_2 after 150 min solar light irradiation.

The regenerability and photostability of the synthesized photocatalyst are crucial parameters for practical applications.
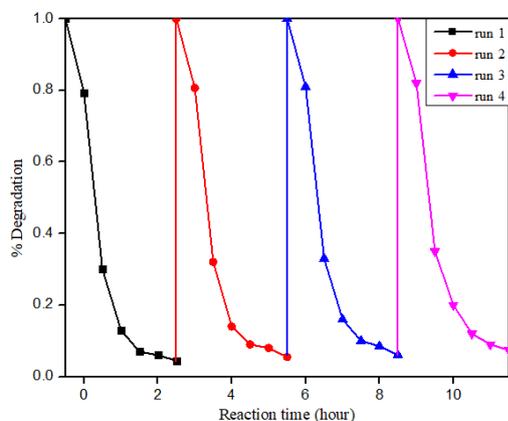

Figure 8: The catalyst regenerability to the degradation of MB dye under solar light.
Reaction conditions: solar light irradiation (=750 lx), environment temperature (30 ^oC), pH=6.5

To evaluate the stability and regenerability of Ag-TiO_2/perlite composite, the MB degradation process using Ag-TiO_2/perlite photocatalyst was repeated 4 times (Figure 8). MB dye degradation efficiency slightly decreased (92%) after 4 consecutive runs. This has proved the stability of the catalyst in photodegradation.

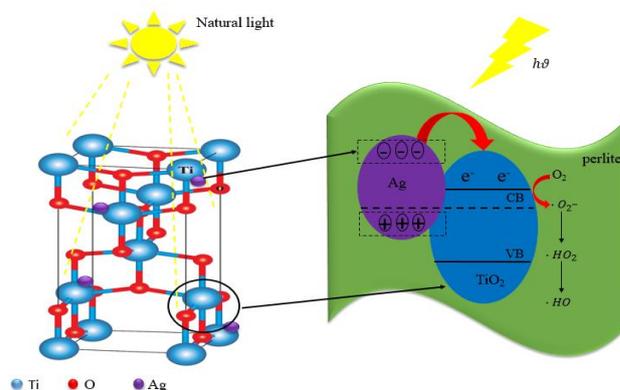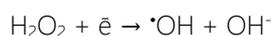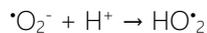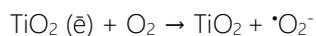The mechanism of MB dye degradation using Ag-TiO_2/perlite as the catalyst is shown in Figure 9.

Figure 9: Schematic illustration of the photocatalytic degradation of MB over Ag-TiO_2/perlite catalyst under solar light irradiation

Perlite, with the advantages of surface area and shrank pore size, helps to adsorb MB to the active phase surface. Then, when irradiating a sufficient solar light source, electrons on Ag will separate from valance band to conduction band, leaving empty orbitals on Ag (h^+). On the other hand, Ag conduction band has higher electronegativity; electrons move from the conduction band of Ag to TiO_2, thereby increasing the separation ability of e^-/h^+ pairs. Under the irradiating of relevant wavelength, electrons and holes transfer to the material surface and interact with some absorbed substances such as water and oxygen to create free radicals on the semiconductor surface like $\cdot OH$ and $\cdot O_2^-$. These free radicals are the main degrading agents of organic compounds. The reactions that took place in the MB photocatalytic process using Ag-TiO_2/perlite as the catalyst are described as follow:

Firstly, under solar light irradiation, electrons in the Ag nanoparticles were photoexcited and Ag^+ ions were formed as the LSPR effect [19].

Ag + visible light (hυ) → Ag$^\bullet$

Secondly, the electric field in the space charge layer promoted the transport of excited electrons from $Ag^{\bullet}$ to TiO_2.

$Ag^{\bullet} + TiO_2 \rightarrow Ag^{\bullet+} (h^+) + TiO_2 (\bar{e})$

$TiO_2 (\bar{e}) + O_2 \rightarrow TiO_2 + {}^{\bullet}O_2^-$

${}^{\bullet}O_2^- + H^+ \rightarrow HO_2^{\bullet}$

$\bar{e} + H^+ + HO_2^{\bullet} \rightarrow H_2O_2$

$H_2O_2 + \bar{e} \rightarrow {}^{\bullet}OH + OH^-$

${}^{\bullet}O_2 + MB \rightarrow$ degraded products

${}^{\bullet}OH + MB \rightarrow$ degraded products

Conclusion

Ag-TiO_2/perlite photocatalyst was synthesized by immobilizing Ag-TiO_2 nanoparticles on perlite granules. Characterization methods have proved that Ag was doped successfully into the structure of TiO_2. The presence of Ag nanoparticles and perlite facilitated the band gap energy reduction, prevents the recombination of the photogenerated electron-hole pairs, which significantly improves the photocatalytic efficiency. Ag-TiO_2/perlite composite has a band gap energy of approximately 2.9 eV, MB degradation efficiency in the water environment reached 95.54 % after 150 min under solar light irradiation. The catalyst was highly stable, achieved an efficiency of 92 % after 4 consecutive runs.

Acknowledgments

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