Preparation of a hybrids APT@MIL by one-step solvent-thermal method for effectively degrading organics

Yaping Zhang, Di Gao, Yufeng He, Bozhen Li, Pengfei Song and Rongmin Wang

ABSTRACT

The attapulgite (APT), a typical clay with shape of nano-rod, was introduced MIL-101(Fe), a typical eco-friendly iron-based Metal-Organic Framework materials (MOFs), during the preparation by one-step solvothermal method, which afforded a novel APT and MOFs hybrids (APT@MIL). Based on the characterization of SEM, FT-IR and XRD, it was found that the rod-like crystals of APT determined the size of MIL-101(Fe) while maintaining its regular octahedral crystal form, and the crystal size of MIL-101(Fe) in APT@MIL enlarged to 4 times. It was also discovered that the rod-like APT were evenly distributed in MIL-101(Fe) crystals. Using APT@MIL as the photocatalyst, some organic dyes were photodegraded in the simulated sunlight. The analysis indicated that APT@MIL has a high adsorption and photodegradation activity, the removal rate of methylene blue got up to 99.5%. Finally, the photocatalytic activity of APT@MIL was verified by UV-Vis DRS, photoluminescence spectra. The thermodynamic adsorption, kinetic characteristics adsorption, and removal mechanism of APT@MIL were also discussed. In summary, a novel hybrid material APT@MIL was successfully prepared with good adsorption and photocatalytic performances. It is expected to be used in photocatalytic degradation of dye wastewater.

Key words | attapulgite, hybrids, MOFs, organics removal, photodegradation

HIGHLIGHTS

- A new hybrid material APT@MIL was prepared by one-step solvent-thermal method.
- APT is not only distributed in MIL-101 (Fe) octahedral crystal, but also maintains the original structure of MIL-101 (Fe) octahedral crystal.
- Compared with MIL-101 (Fe), the crystal size of APT@MIL increased to 4 times.
- The formation mechanism of APT@MIL was studied.
- The hybrid material has high efficiency in the remove of methylene blue wastewater.
INTRODUCTION

Being accompanied by the process of industrialization, human beings are faced with two major challenges of resource shortage and environmental pollution. Among all the challenges, the water body is polluted by the organic dyes, antibiotics and others, which not only damage the environment seriously, but also cause a major threat to human health (Rattee et al. 2015; Wang et al. 2013). Many materials and technologies had been developed for dealing with organic pollutants (Crini & Lichtfouse 2013; Bao et al. 2013; Gunture et al. 2020). The use of renewable solar energy can promote photocatalytic reactions under the mild conditions and provide an economical and effective technical approach for the degradation of water pollutants (Zhou et al. 2016; Su et al. 2018). Semiconductor materials are widely used in photocatalysis because of their good conductivity and adjustable band gap energy (Sharma et al. 2019). Thus, many semiconductor photocatalysts had been prepared (Shen et al. 2015; Tan et al. 2019). Meanwhile, Metal-Organic Framework materials (MOFs) are also typical photocatalysts, which has many advantages in improving the generation, separation and utilization of electron-hole pairs, such as high structural designability, porosity, crystallizability and structural diversity (Zhou et al. 2010; He et al. 2014). Therefore, many kinds of MOFs have been synthesized and applied in water treatment, for instance, MILs, UiOs, ZIFs and HKUST. Among them, MIL-101(Fe) is a non-toxic and environmentally friendly three-dimensional porous solid, which was built up by 1,4-Bezenedicarboxylate (H₂BDC) linker and FeO₄(OH)₂ octahedra, is a visible light-responsive photocatalyst for the degradation of organics (Liang et al. 2015) and CO₂ reduction (Ai et al. 2014), which provides more active sites for the photocatalytic reaction (F. Millange et al. 2010; Cunha et al. 2013). In another side, the attapulgite (APT), also known as palygorsite (PL), is a kind of clay with rod or fibrous structure, which shows large specific surface area, adsorption capacity, good rheological property and catalytic performance. It has been used as carriers to prepare adsorbent (Mu & Wang 2016), and supporters for the photocatalysis (Zuo et al. 2017; Xu et al. 2018). However, there are few reports about using APT as active ingredients for prepare functional hybrids.

In this study, the APT, a typical eco-friendly and low-cost clay with nano-rod structure, was used to improved adsorption and photocatalytic activity of iron-based MOFs. Being different common modification methods, the dispersion liquid of pretreated APT was added into the precursor solution of MIL-101(Fe). Then, a novel hybrids (APT@MOFs) obtained with solvothermal reaction. Based on SEM, FT-IR, XRD and Zeta potential test, the structure and the formation mechanism of hybrids was investigated. The removal performance of APT@MOFs to organics was discussed by measuring UV-Vis DRS and PL. Adsorption and photocatalytic degradation of organic dyes by APT@MIL was studied and removal mechanism was also discussed.

EXPERIMENTAL

Materials and reagents

Attapulgite (APT) was purchased from Xuyi Aobaite Clay Material Co., Ltd. Potassium thiocyanate (KSCN, ≥98.5%)
was obtained from Tianjin Yaohua Chemicals. Other chemical reagents with analytical grade, such as ferric chloride hexahydrate (FeCl₃·6H₂O) (Tianjin Beishi Chemicals), 1,4-benzenedicarboxylate (H₂BDC) (Aladdin Reagent Co. Ltd), N,N-dimethyl formamide (DMF) (Lanzhou Gongyi Electronic Commerce Co., LTD), anhydrous ethanol (EtOH) (Sinopac Chemical Reagent Co., LTD), methylene blue (MB) (Tianjin Deen Chemical Reagent Co., LTD), malachite green (MG) (Beijing Institute of Chemical Reagents), crystal violet (CV) (Beijing Chemical Plant), RhB (Tianjin New Fine Chemical Development Center) were acquired commercially. The redistilled water was used throughout the experiment.

Synthesis of APT@MIL

APT@MIL hybrid was prepared by one-step solvothermal method, specifically as follows: Firstly, 1.76 g APT was dispersed in 30.0 mL DMF with ultrasonic treatment for 15 min. 1.35 g FeCl₃·6H₂O and 0.41 g H₂BDC were added and stirred until dissolved. Secondly, the mixture was transferred to a teflon-lined stainless-steel reactor, and reacted for 20 h at 110 °C. Then, the reaction mixture was cooled down to room temperature. The dark orange solid was acquired by centrifuging. Soaked the obtained crude products in hot ethanol (60 °C) for 3 h and centrifuged for 2 times, and then washed with DMF and ethanol for 3 times, respectively. Finally, the solid product was dried for 30 min under 70 °C, and then activated for 8 h at 150 °C, a novel hybrid (APT@MIL-x) was obtained. The formula for preparation of APT@MIL-x with different ratios of APT@MIL was showed in Tab S1.

The pure MIL-101(Fe), a typical MOFs containing Fe, was also prepared with reported method (Wang et al. 2018) for comparing with APT@MIL. SEM, FT-IR and XRD were used for structural characterization and performance analysis. Then, its photoluminescence spectra (PL) were used to determine the photoluminescence rate of the photocatalyst.

Photocatalytic activity

The photoreactivity of the obtained catalyst (APT@MIL) was evaluated by photodegradation of dyes under the simulated sunlight using a high-pressure xenon lamp (800 w). A UV cut-off filter (664 nm) was applied to remove UV light for the test of photocatalytic activity in the visible light region (420–800 nm). Typically, 0.02 g of APT@MIL was added to 50 mL of methylene blue (MB) solution ([MB]: 20 mg/L). After stirring 30 min in darkness, the adsorption-desorption equilibrium of organics was established.

Then, photodegradation of antibiotics was performed under light. At set intervals, the samples were withdrawn from the reactor and filtered by PES syringe filter (pore size: 0.22 μm) for the removal of photocatalyst particles. Finally, the content of residual MB was determined by UV-Vis spectrophotometer. Using APT@MIL as photocatalyst, the photodegradation performance of organics was tested with the same method.

RESULTS AND DISCUSSION

A novel APT and iron-based MOFs hybrid (APT@MIL) was prepared through one-step solvent-thermal method (Figure 1). In addition, pure MIL-101(Fe) was also prepared with reported method (Wang et al. 2018) for comparing with APT@MIL. SEM, FT-IR and XRD were used for structural characterization and performance analysis. Then, its...
adsorption and photocatalytic activity for removal of organics in wastewater was investigated.

**Morphological analysis**

The microtopography and surface of APT@MIL was characterized by scanning electron microscopy (SEM), and results were showed in Figure 2. In the image of APT (Figure 2(a)), there are some bundles or aggregates which indicated that the severe agglomeration of APT due to Van der Waals forces and hydrogen bond interactions, was consistent with literature reports (Xu et al. 2014). MIL-101(Fe) is a regular octahedron with special microstructure, and crystal size ranges from 400 to 550 nm (Figure 2(b)), which is very similar to the reported reports (Chi et al. 2016; Li et al. 2016). It indicated that MIL-101(Fe) had been successfully prepared. In APT@MIL (Figure 2(c)), adding APT into the precursor solution of MIL-101(Fe), the crystal shape and octahedral structure of MIL-101(Fe) was maintained, but its size increased 4 times (from 500 nm to 2 μm). Moreover, APT nano-rod was distributed on the surface of MIL-101(Fe) crystal. It showed that the hybrid of APT and iron-based MOFs (APT@MIL) was successfully prepared.

The macroscopic feature was also observed (Fig. S1). Among them, the obtained APT@MIL (Fig. S1c), which APT was supported by MIL-101(Fe) photocatalyst, was a gray-brown powdery particle. It was lighter than MIL-101(Fe) (Fig. S1b), and darker than APT (Fig. S1a). It Indicated APT was supported to MIL-101(Fe), facilitating the absorption of light by the catalyst, which was consistent with SEM results.

**FT-IR analysis**

The infrared spectra (FT-IR) of APT@MIL and its raw material, MIL-101(Fe) and APT, were showed in Figure 3. The absorption peak of MIL-101(Fe) corresponds to the locations of 1,704, 1,596, 1,391, 750 and 547 cm⁻¹. Among them, the peak at 1,596 cm⁻¹ and 1,391 cm⁻¹ are assigned to carbonyl stretching vibration asymmetric and symmetric stretching vibration peak. The peak at 750 cm⁻¹ corresponds to the C-H bending vibration of benzene, and vibration of Fe-O appears near 547 cm⁻¹. A very wide peak in the range of 3,600-3,100 cm⁻¹ was due to the hydroxyl (-OH) of H₂O. The results of MIL-101(Fe) in this experiment are consistent with those in the literature (Tang et al. 2015). The absorption peaks of APT at 1,037, 804 and 481 cm⁻¹ were attributed to the stretching vibration peak of Si-OH, and 467 cm⁻¹ was attributed to the vibration peak of O-Si-O, which are also consistent with those in literatures (Wang et al. 2017; Zhao et al. 2019). In APT@MIL, the characteristic absorption peaks of both MIL-101(Fe) and APT exist which means the hybrid material of clay and MOFs was successfully prepared.

**XRD analysis**

The XRD patterns of the APT@MIL and its raw materials, MIL-101(Fe) and APT, were showed in Figure 4. The peaks of MIL-101(Fe) are consistent with the reported results by Tang (Tang et al. 2015) and Skobelev (Skobelev et al. 2013), and the characteristic peaks appeared at 2θ = 8.6°, 8.9°, 10.2°, 10.6° and 16.4° (Wang et al. 2014). The characteristic peak of APT appeared in 2θ = 8.4°, 13.7°, 19.6°, 20.8°, 28.0° and 30.9°, corresponding to (110), (200), (040), (121), (400) and (331) crystal surfaces of attapulgite (JCPDS No. 31-0783), respectively. In addition, other characteristic peaks were related to quartz (JCPDS No. 46-1045) in APT (He et al. 2018). From the XRD pattern of the hybrid material, it could conclude that the crystal structure of APT and MIL-101(Fe) were maintained by the photocatalyst APT@MIL, which are same with results of SEM. It further proved that the addition of APT did not affect the crystal frame of MIL-101(Fe).

**UV-Vis DRS and photoluminescence analysis**

APT@MIL, pure MIL-101(Fe) and APT were analyzed by ultraviolet-visible diffuse reflectance (UV-Vis DRS) to...
verify their photocatalytic performance, and results are shown in Figure 5. In APT@MIL and MIL-101(Fe) (Figure 5(a)), there is a strong absorptive band in the range of 200 nm ~ 400 nm, and assigned to the ligand-to-metal charge transfer in MIL-101(Fe) (Islam et al. 2016). In MIL-101(Fe), the absorption band in visible range of 400 nm ~ 600 nm, which is attributed to the d-d charge transfer of Fe-O clusters in MIL-101 (Nguyen et al. 2020), slightly increased in hybrids (APT@MIL). The formation of hybrids can improve the absorption of visible light, thereby enhancing the photocatalytic activity of the hybrid material.

The photoluminescence (PL) emission spectrum is widely used to study the efficiency of carrier capture, migration and transfer (Salavati-Niasari et al. 2019). The recombination rate of photoexcited electron-hole pairs can be indicated by PL spectra. Generally, the stronger intensity of photoluminescence emission suggests a higher recombination rate of electrons and holes (Meng et al. 2019). In Figure 5(b), the APT@MIL showed emission peaks near 400 nm, which corresponded to the DRS analysis results. Compared with APT and MIL-101(Fe), the hybrids (APT@MIL) showed lower fluorescence emission intensity. It indicated that the synergistic effect of APT and MIL-101(Fe) was beneficial to the inhibition of photoelectron-hole pair recombination (Thanh et al. 2019), thus improving the photocatalytic activity of hybrid material.

**Formation mechanism of APT@MIL**

The growth mechanism of hybrids (APT@MIL) was suggested as Figure 1, and confirmed by measuring Zeta potential (Figure 6). Before preparing MOFs, the nano-rod APT was added to the precursor solution of MIL-101(Fe), and was fully dispersed in the solution through ultrasonic and constant stirring. In the solvent-heating reaction process, a few part of Fe$^{3+}$ (supplied by FeCl$_3$·6H$_2$O) in the solution attached to the APT surface containing negative
charges and then coordinated with carboxylate anions (-COO-), being supplied by H2BDC, to form regular octahedral structure. Most of Fe$^{3+}$ ions in the solution coordinated with carboxylate and self-assembled, which formed the regular octahedral structure of MIL-101(Fe) and hybrid with the APT nano-rod. The surface charge of pure MIL-101(Fe) and APT was measured. It was confirmed that the surface of MIL-101(Fe) is positively charged (Zeta potentials: +33.6 mV) (Figure 6(a)), and APT surface was negatively charged (Zeta potentials: −8.8 mV) (Figure 6(b)). Therefore, APT can easily bind to its surface in situ through electrostatic induction self-assembly (Liang et al. 2018). In APT@MIL with a regular octahedral structure, the APT nano-rod is uniformly distributed on each crystal plane of the MIL-101(Fe). Due to the Ostwald Ripening effect, MIL-101(Fe) keeps its original octahedral crystal form. But the crystal size of MIL-101(Fe) in APT@MIL enlarges to 4 times.

**The adsorption and photocatalytic performance of APT@MIL**

Some typical dyes (MB, RhB, CV, MG) were selected as the targets, and the adsorption and photocatalytic degradation performance of APT@MIL was investigated under the same experimental conditions (cat: 0.02 g, substrate concentration: 50 mg/L, lighting 80 min) with the simulated sunlight. The results were shown in Table 1. Being compared with the other three dyes (RhB, CV, MG), APT@MIL has the best activity for MB, and its removal rate got up to 99.5%.

In order to investigate to relationship between APT and MIL in APT@MIL, a series of hybrids were prepared with changing ratios of APT/MIL-101(Fe) (Tab S1). Moreover, their removals of MB were measuring. The results were showing in Table 2. Among them, APT@MIL, APT: MIL being 1.0: 1 (g: g), had the highest removing efficiency for MB, with removal rate was up to 99.5%. It is higher than that of reported photocatalyst, MoS2/Cu/TiO2 nanoparticles (Santos et al. 2018). With adding more APT, its removal efficiency began to decline. In summary, APT@MIL, the optimal proportion of APT: MIL being 1.0: 1(g: g), was selected as the optimal preparation condition of hybrid material for subsequent experiments.

![Figure 6](image_url) The Zeta potential of MIL-101(Fe) (a) and APT (b).

| Table 1 | Removal rate of MIL-101(Fe), APT and APT@MIL for four different dyes |
|---------|-----------------------------|
|         | MB    | RhB   | CV    | MG   |
| APT@MIL | 99.5% | 98.4% | 88.6% | 75.2%|
| MIL-101(Fe) | 57.8% | 99.9% | 66.2% | 78.6%|
| APT     | 74.0% | 81.4% | 82.1% | 46.7%|

| Table 2 | Effect of main raw material ratio on photocatalytic performance of product APT@MIL-101 |
|---------|---------------------------------------------|
| No      | APT/MIL (g:g) | Yield (%) | Removal rate (%) |
| APT     | 1.0: 0        | 96.0      | 74.0            |
| MIL-101(Fe) | 0: 1.0    | 23.0      | 57.8            |
| APT@MIL-0.5 | 0.5: 1    | 36.9      | 96.1            |
| APT@MIL | 1.0: 1        | 47.0      | 99.5            |
| APT@MIL-1.5 | 1.5: 1    | 45.8      | 86.0            |
| APT@MIL-2.0 | 2.0: 1    | 54.3      | 80.4            |
The adsorption and photocatalytic degradation performance of APT@MIL were investigated by the removal of MB and compared with MIL-101(Fe) and APT at different times. The results were shown in Figure 7. It indicated that MB was rarely self-degrading in the absence of photocatalyst (Figure 7(a)). The synthesized hybrids, APT@MIL, presented excellent adsorption and photocatalytic degradation. The adsorption rate of MB under darkness was 79.2% within 40 min, and its removal rates got to 99.5% after being illuminated 80 min under the simulated sunlight. It was higher than that of MIL-101(Fe) (41.7%) and APT (68.2%). The results showed that the APT@MIL, a typical hybrid of MIL-101(Fe) and APT, achieved a synergistic effect through APT adsorption of pollutants and MIL-101(Fe) photocatalysis, which shown a excellent catalytic removal efficiency for organics under visible light irradiation.

The electronic spectra analysis was performed on measuring degraded MB solution by APT@MIL at different time periods, and the results are shown in Figure 7(b). It indicated that the maximum absorption peak appears at the wavelength of 664 nm. With increasing the photodegradation time, the absorption peak intensity gradually weakened. That means the concentration of MB solution gradually reduced. Additionally from −40 min (the beginning of the adsorption) to 0 min (the end of the adsorption and the beginning of the light reaction), the intensity of the absorption peak changed greatly. It indicated that adsorption played a major role in the whole dye removal process. Therefore, the adsorption characteristics will further be discussed in the subsequent experiments.

Some affected factors on adsorption and photodegradation of MB were investigating, such as catalyst dosage, initial MB concentration, pH value of the solution, and irradiation time, and the results were showing in Fig. S2 and Fig. S3. The optimal initial concentration of MB solution was 50 mg/L, 80 min was selected as the best lighting time, no further pH adjustment was is required for this experiment.

In order to prove the optimal amount of photocatalyst, the kinetics of APT@MIL with different amounts was studied. It was assumed that all reactions followed the pseudo-first-order kinetics model. The calculation formula was shown in Equation (1):

\[ \ln \left( \frac{C_0}{C} \right) = k t \]

where, t(min)-reaction time; The concentration of solution reached the adsorption-desorption equilibrium after C0(mg/L)-30 min. C(mg/L)-the concentration of the solution in the reaction system at time T; K(min\(^{-1}\))-relative removal rate constant, whose value is equal to the slope of \(\ln \left( \frac{C_0}{C} \right)\) and the time curve. The results are shown in Fig. S2 (b). The rate constants of catalysts with different dosage are 0.02 g (0.0087 min\(^{-1}\)) > 0.01 g (0.0024 min\(^{-1}\)) > 0.04 g (0.0053 min\(^{-1}\)) = 0.025 g (0.0053 min\(^{-1}\)) > 0.05 g (0.0046 min\(^{-1}\)) > 0.03 g (0.0045 min\(^{-1}\)) > 0.015 g (0.0045 min\(^{-1}\)) > 0.01 g (0.0024 min\(^{-1}\)). It indicated that 0.02 g is the optimal amount of photocatalyst.

**Adsorption kinetics and thermodynamics of APT@MIL**

The Freundlich and Langmuir isothermal adsorption model were employed to study the adsorbent adsorption process.
The Freundlich model is an empirical model to describe heterogeneous adsorption systems, which describes the exponential distribution of heterogeneous adsorbent active sites and their related adsorbent energy (Freundlich et al. 1926). Langmuir model describes a series of monolayer adsorption behaviors at different adsorption sites under the assumption of surface uniformity of adsorbent (Langmuir 1918). The nonlinear expressions of isothermal adsorption model are Freundlich (Equation (1)) and Langmuir (Equation (2)).

\[
q_e = K_f C_e^{1/n}
\]

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e}
\]

Here, \(C_e\) (mg/L): the concentration of adsorbents in the solution at adsorption equilibrium. \(K_f\): freundlich isothermal adsorption empirical constant, related to adsorption capacity and adsorption strength. \(q_e\): (mg/g) adsorption capacity per unit mass APT@MIL at equilibrium. \(q_m\) (mg/g): Unit mass APT@MIL maximum monolayer adsorption. It was believed that the value of \(1/n\) is between 0 and 1, which indicated the strength of the influence of concentration on adsorption capacity. The smaller \(1/n\), the better adsorption performance will be. \(K_L\) (L/mg) is the isothermal adsorption energy constant of Langmuir. When \(K_L > 1.0\), it is not a monolayer adsorption; When \(K_L = 1.0\), there is a linear relationship; Monolayer adsorption occurs when \(K_L < 1.0\). It’s irreversible adsorption when \(K_L = 0\).

The results are shown in Figure 8 and Tab. S2. According to these data, the correlation coefficients \(R^2\) of the Freundlich and Langmuir isothermal adsorption model fitting were 0.9718 and 0.8037, respectively. It indicated that the experimental data presented a good nonlinear correlation with the trend line obtained by the Freundlich isothermal adsorption model fitting. Comparing with the Langmuir isothermal adsorption model, APT@MIL was more in line with the Freundlich isothermal adsorption model, indicated that the adsorption of MB by APT@MIL was not a single monolayer adsorption. The parameter \(N\) obtained by Freundlich model fitting shows that \(1/n\) is small, which indicated that APT@MIL has a relatively good adsorption capacity for MB.

Through the pseudo-first-order kinetic model and pseudo-second-order kinetic model proposed by Lagergren, the adsorption kinetic characteristics of APT@MIL for MB were also studied. The nonlinear expressions of the two models are Equations (3) and (4), respectively.

\[
q_t = q_e(1 - \exp^{-K_1 t})
\]

\[
q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t}
\]

In the above formula, \(t\) (min) adsorption time; \(q_t\) Adsorption capacity of \(t\); \(q_e\) (mg/g) is the adsorption capacity at adsorption equilibrium; \(K_1\) (or min\(^{-1}\) or h\(^{-1}\)) and \(K_2\) (mg·g\(^{-1}\)·min\(^{-1}\)) shall be the different first-order kinetic rate constant and the second order kinetic rate constant.

The results are shown in Figure 9 and Tab. S3. The correlation coefficient \(R^2\) obtained by the nonlinear fitting is 0.9904 and 0.9842, respectively. The theoretical calculation the adsorption quantity of \(q_{e,cal}\) value (118.48 mg/g) and the data from experiment (98.35 mg/g) was closer. It indicated that APT@MIL adsorption kinetics characteristics of MB are more accord with the first order kinetics model, namely, physical adsorption is the dominant.
The mechanism for removing dyes by APT@MIL

Based on the characterization, it was confirmed that nanorod of APT was in situ and evenly combined with MIL-101(Fe), which afforded the hybrid of APT@MIL (Figure 1). It effectively avoids the reunion of APT stick crystals. The hybrid not only improves the stability of the obtained material (APT@MIL), but also increases its specific surface area and active sites.

The mechanism for removing dyes by APT@MIL was suggested as Figure 10. After comparing with APT, through the adsorption of the organic pollutants are easy to be absorbed near the photocatalytic active centers of MOF. The APT@MIL presents the synergistic effect of adsorption and photocatalytic degradation performance in visible light, which improves the removal rate of organics During photocatalytic degradation process, MIL-101(Fe) was activated by light to produce e\(^-\) and h\(^+\). Because Fe(III) in the Fe-O cluster can easily capture electron (e\(^-\)) in the conduction band and be reduced to Fe(II). At the same time, the h\(^+\) generated by the valence band oxidize OH\(^-\) in the water to \(\cdot\)OH, which further degrade the organics in the solution into pollution-free substances. Therefore, the MB molecules in the solution were degraded by the generated \(\cdot\)O\(^2-\) and OH. In summary, APT@MIL degradation of organics was due to the synergistic effect of APT adsorption and MIL-101(Fe).

Recycle test

In order to test the cyclic stability of APT@MIL, the following experiments were carried out: A batch of 50 mL of MB solutions (50 mg/L) were added with 0.02 g APT@MIL respectively. The photocatalytic reaction was conducted for 80 min at room temperature. After each operation under the above conditions, the photocatalyst was collected by centrifugation, washed by distilled water and ethanol for 6 times, and finally dried for 5 h in a vacuum oven at 60 \(\degree\)C. The results were shown Figure 11. After being cyclic used for 5 times, the removal rate of MB decreased from 99.5% to 90.0%.

In order to prove photocatalytic mechanism and analyzing reason of activity declines of photocatalyst, the recovered APT@MIL was characterized by XRD. Comparing with the fresh hybrid (APT@MIL), there has few changes. After the photocatalytic reaction, which confirmed that APT@MIL hybrid material has good structural stability. In addition, the leaching of iron ions (Fe\(^{3+}\)) was measured with reagent color-developing method, and potassium thiocyanate (KSCN) was used to test the dissolution of iron ions. It showed that iron ions was not detected after 2–3 cycles. And only very few Fe\(^{3+}\) ions was detected after 4 and 5 cycles. It suggested the reason of activity declines is a little iron ion leaching.

It was confirmed that APT@MIL hybrid material has good structural stability and recycling efficiency in photocatalytic degradation of MB because there is a close contact
interface between MIL-101(Fe) and APT, and its structure can maintain good integrity in the process of photocatalysis.

CONCLUSION

A novel APT and MOFs eco-friendly hybrids (APT@MIL) was successfully prepared by one-step solvothermal method. MIL-101(Fe), a kind of non-toxic and low-cost MOFs, was combined with economically and environmentally friendly APT. The obtained APT@MIL showed excellent activity of removing organics in wastewater because of the synergistic effect through the adsorption of pollutants by APT and the photocatalysis of MIL-101(Fe). Therefore, APT@MIL, a novel of inexpensive, efficient and eco-friendly hybrids, has a widely application prospects in photocatalytic degradation of organic wastewater.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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