available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Facile preparation of sepiolite@LDH composites for the visible-light degradation of organic dyes

Li Jin, Hong-Yan Zeng*, Sheng Xu, Chao-Rong Chen, Heng-Zhi Duan, Jin-Ze Du, Guo Hu, Yun-Xin Sun

College of Chemical Engineering, Xiangtan University, Xiangtan 411105, Hunan, China

ARTICLE INFO

Article history:

Received 15 April 2018

Accepted 4 June 2018

Published 5 November 2018

Keywords:

Layered double hydroxides

Sepiolite

Photocatalytic performance

Water treatment

Nano materials

ABSTRACT

Sepiolite@LDH (Sep@LDH) composites were designed and prepared based on the assembly of layered double hydroxides (LDH) on acidified sepiolites (Sep) for the simultaneous photocatalytic degradation of methyl orange (MO) and methylene blue (MB). The structure, morphology, texture, optical properties, and photocatalytic performance of the prepared Sep@LDH were studied in detail. Among the Sep@LDH composites, Sep₄@LDH (4.0 g Sep) exhibited the highest photocatalytic activity under visible-light irradiation, which could be attributed to its large surface area, high crystallinity, and plentiful active sites on its surface. The photodegradation of the dyes followed a pseudo first-order kinetic model (Langmuir-Hinshelwood model), indicating that the copious and homogeneous active sites on the surface of the composites contributed to the high photocatalytic activity. The photodegradation mechanism was studied by examining the active species ($\bullet\text{OH}$, h^+ , and $\bullet\text{O}_2^-$ anions) using appropriate scavengers. It was found that $\bullet\text{OH}$ radicals played a critical role in the photocatalytic process of MO and MB, where the generation of $\bullet\text{OH}$ radicals occurred on the electron/hole (e^-/h^+) pairs on the surface of the Sep@LDH composites.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Persistent and non-biodegradable organic substances, such as organic dyes, are dangerous to the ecosystem and human health [1]. Due to their complex structure, removing dyes from industrial wastewater by traditional methods including adsorption, coagulating sedimentation, chemical oxidation, and biological digestion is not effective [2,3]. Photocatalysis is an oxidative process that has been established as one of the most useful and environmental friendly methods for the degradation of dye pollutants [4]. Among the materials used for the photocatalytic degradation of dye pollutants, semiconducting layered double hydroxides (LDH) with easily tunable chemical compo-

sition have attracted increasing attention as a class of anionic clay materials, because of their high adsorption and photocatalytic activity. A diverse range of transition metal ions can be stabilized in the octahedral sites of the LDH lattices [5,6,32]. Especially, ZnCr-LDH exhibited a fairly high photocatalytic activity for the UV light-induced generation of orange II and 4-chlorophenol [7], and for the photodegradation of the dyes (rhodamine B, rhodamine 6G) under visible light [8]. However, the application of ZnCr-LDH materials is limited by their aggregation tendency, weak adsorption, and difficult separation from wastewater [9].

Sepiolite, a hydrated magnesium silicate clay mineral, is fibrous, has a theoretically large surface area, and high

* Corresponding author. Tel: +86-731-58298175; E-mail: hongyanzeng99@hotmail.com, hyzeng@xtu.edu.cn

This work was supported by the Joint Research Program of Hunan Provincial Natural Science Foundation (Xiangtan) of China (2016JJ5030), Hunan 2011 Collaborative Innovation Center of Chemical Engineering & Technology with Environmental Benignity and Effective Resource Utilization and General project of Hunan Provincial Education Department (17C1526), PhD Startup Foundation of Xiangtan University (17QDZ05), and Xiangtan University undergraduate innovative experiment program (2017XJ067).

DOI: 10.1016/S1872-2067(18)63120-1 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 11, November 2018

chemo-mechanical stability [10], which are related to the powerful adsorbent properties for organic or inorganic molecules and ions [1]. Sepiolite has been studied as an effective material for the photocatalytic treatment of pollutants due to its unique properties and structures as well as its abundance and low cost [11]. For example, a TiO_2 -supported sepiolite composite showed high photocatalytic activity for gaseous formaldehyde degradation under UV light, and a positive synergistic effect on TiO_2 photocatalysis was observed [12]. Akkari et al. [13] prepared $\text{ZnO}/\text{Fe}_3\text{O}_4$ -sepiolite composites for degrading methylene blue dye under UV light and the composites exhibited good photoactivities and superparamagnetic properties. Thus, sepiolites are ideal carrier materials for the ZnCr-LDH catalyst, which can improve catalyst adsorption capacity and separation from wastewater.

In this study, acid-activated sepiolite (Sep) served as a carrier for ZnCr-LDH , which was assembled on the surface of the Sep by *in situ* co-precipitation to prepare the composites (Sep@LDH). To determine the photocatalytic performances of the prepared Sep@LDH, methyl orange (MO) and methylene blue (MB) were chosen as model pollutants present in the same solution. The structure, morphology, texture, and optical features of the composites were determined by X-ray diffraction (XRD), Scanning electron microscopy (SEM), N_2 adsorption-desorption, Thermogravimetry and differential thermal gravity (TG/DTG), Ultraviolet-visible diffuse reflectance spectra (DRS) and Photoluminescence (PL) analyses. The photocatalytic performances of the composites were evaluated and compared for degradation of the two co-existing dyes under visible-light irradiation. The photodegradation mechanism of Sep@LDH was proposed based on the contribution of specific scavengers and kinetics of the photocatalytic reaction of co-existing MO and MB. Moreover, to the best of our knowledge, few reports have been published regarding the photocatalytic performances of Sep@LDH photocatalysts under visible light.

2. Experimental

2.1. Materials

MO, MB, and other reagents were of analytical grade (AR) and used without further purification, as-received from Nan-Jin Chemical Reagent Co., Ltd. (China). All solutions were made with deionized water, and $0.1 \text{ mol}\cdot\text{L}^{-1}$ NaOH and HCl solutions were used for pH adjustments. A pH electrode (Mettler Toledo S40K) was used for pH measurements.

Raw sepiolite was purchased from Xiangtan YuanYuan Sepiolite New Materials Co. Ltd. (Hunan, China), and the physico-chemical properties of the sepiolite are listed in Table S1. The sepiolite was treated before the experiments as follows: the suspension containing $10 \text{ g}\cdot 100 \text{ mL}^{-1}$ sepiolite was mechanically stirred for 5 h in a HCl solution ($1.0 \text{ mol}\cdot\text{L}^{-1}$). After waiting for approximately 3 min, the supernatant suspension was filtered, washed until a neutral pH was reached with deionized water to remove the excess Cl^- , and then dried at 80°C for 24 h. The solid sample was ground and sieved using a 200-mesh

sieve for further experiments, and the pre-acidified sepiolite was denoted as Sep.

2.2. Self-assembly of the ZnCr-LDH onto the Sep

The sepiolite@LDH composites were prepared using *in situ* co-precipitation (Scheme 1). First, solution A (200 mL) was prepared by mixing solutions of Zn and Cr nitrates with a Zn/Cr molar ratio of 1.0 ($\text{Zn}^{2+} + \text{Cr}^{3+} = 1.2 \text{ mol}\cdot\text{L}^{-1}$). Solution B was prepared by dissolving NaOH ($1.75 \text{ mol}\cdot\text{L}^{-1}$) and Na_2CO_3 ($0.75 \text{ mol}\cdot\text{L}^{-1}$) in 200 mL of deionized water, and 100 mL suspension solution containing different amounts of Sep was prepared. Subsequently, the A and B solutions were added simultaneously to the Sep suspension solution at 60°C under vigorous stirring for 3 h. The precipitate was aged at 80°C for 12 h, filtered and washed until the pH was neutral, and subsequently dried at 90°C for 24 h to obtain the resulting sample that was denoted Sep@LDH. For convenience, the samples produced with different Sep masses (1.0, 2.0, 4.0, 6.0, and 10.0 g) in the 100 mL suspension solution were designated as Sep₁@LDH, Sep₂@LDH, Sep₄@LDH, Sep₆@LDH, and Sep₁₀@LDH, respectively.

For comparison, the ZnCr-LDH samples with Zn/Cr molar ratios of 0.5, 1.0, and 2.0 were also prepared by co-precipitation. The preparation procedure was similar to that of the Sep@LDH without the Sep suspension, where solutions A and B ($\text{Zn}^{2+} + \text{Cr}^{3+} = 1.2 \text{ mol}\cdot\text{L}^{-1}$) were added simultaneously to a beaker under vigorous stirring. In preliminary work, the ZnCr-LDH with a Zn/Cr molar ratio of 1.0, designated as LDH, was determined to be the best candidate due to its low band-gap energy in the visible-light region, large surface area, and weak electron-hole recombination (Figs. S1 and S2). It also exhibited the highest photocatalytic activity in the solution of co-existing MO and MB dyes (Fig. S3). Thus, solution A was prepared by mixing an equal molar ratio of Zn^{2+} and Cr^{3+} for the preparation of Sep@LDH.

2.3. Photocatalytic test

The photocatalytic performance of the prepared samples was evaluated in synthetic wastewater containing equal concentrations of MO and MB under visible light as a model reaction. Various amounts of catalyst in synthetic wastewater were magnetically stirred in the dark for 30 min to reach adsorption-desorption equilibrium, and were then exposed to visible light from a 300W Xe lamp equipped with a UV cutoff filter ($\lambda \geq 420 \text{ nm}$) at a specific time. A 3mL aliquot of the reaction solution was withdrawn by a syringe at given time intervals and

Scheme 1. Sepiolite@LDH composites prepared using *in situ* co-precipitation.

centrifuged to remove the catalyst for dye concentration measurement. A control reaction was performed following the same procedure without adding any catalyst. All results were obtained and reported with reference to the corresponding controls. The concentrations of the two dyes were determined by measuring the absorbance at characteristic wavelengths by UV-vis spectrophotometry (Hitachi U-2910), where the $\gamma_{\max}$ values were 465 nm for MO and 665 nm for MB (Fig. S4). The MO (or MB) removal ratio (degradation and adsorption ratio) was determined using the following equation:

$$\eta_{\text{MO,MB}}(\%) = \frac{C_0 - C_t}{C_0} \times 100\%$$

where η is the removal ratio (%), C_0 is the initial concentration of MO (or MB), and C_t is the concentration ($\text{mg}\cdot\text{L}^{-1}$) at time t (min).

2.4. Characterization of photocatalysts

Powder XRD measurements were performed using a Japan Rigaku D/max 2550PC ($\lambda = 1.5405 \text{ \AA}$) instrument with Cu $K\alpha$ irradiation. The scan step was 0.02° (2θ) with a filament intensity of 30 mA and a voltage of 40 kV. SEM (JEOL JSM-6700F) was used to characterize the surface morphology of the samples. The specific surface area, pore volume, and diameter of the samples were determined by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Hallender (BJH) methods using a NOVA-e1000 system (Quantachrome, USA). TG/DTG were performed under a nitrogen atmosphere using a Seiko 6300 TG/DTG instrument with a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ under a He stream ($60 \text{ mL}\cdot\text{min}^{-1}$). UV-visible DRS were measured using a UV-visible spectrophotometer (Shimadzu UV-2550, Kyoto, Japan). PL spectra were recorded at room temperature using a F-4600 spectrophotometer at an excitation wavelength of 290 nm.

3. Results and discussion

Fig. 1. XRD patterns of the pure Sep, virgin LDH, and Sep@LDH composites.

3.1. Characterization of the Sep@LDH composites

3.1.1. XRD analyses

The XRD spectra measured for the pure Sep, virgin LDH, and Sep@LDH composites are shown in Fig. 1. The virgin LDH displayed a typical of ZnCr-LDH structure with sharp and intense (003), (006), (009), (110), and (113) reflections, and no other crystalline phase was observed [5]. The XRD patterns of the pure Sep and Sep@LDH composites clearly showed a sepiolite phase, indicating that the sepiolite structure was maintained despite the less intense reflections with an unstable baseline. The XRD patterns of the Sep@LDH composites indicated the presence of ZnCr-LDH and sepiolite. For the Sep₁₀@LDH sample, reflections distinctive of sepiolite were observed, albeit with weak reflections from the crystalline phase of the ZnCr-LDH, implying that the sepiolite structure was the main phase. Compared to the Sep₁@LDH, Sep₂@LDH, and Sep₆@LDH composites, the Sep₄@LDH sample exhibited more intense reflections with a more stable baseline, especially for the (110) and (113) reflections which were more clearly distinguished. This indicated that the Sep₄@LDH sample had a more regular layered structure and higher crystallinity [14].

3.1.2. SEM analyses

Fig. 2 depicts the morphology of the pure Sep and Sep@LDH composites, where the ZnCr-LDH lamellar structure and sepiolite filler are clearly distinguished in the SEM images. The pure Sep exhibited a fibrous morphology and numerous fibers were congregated into bundles. From the SEM images of the Sep@LDH composites, ZnCr-LDH was observed to assemble on the surface of the Sep. The Sep₁₀@LDH exhibited a morphology featuring a ZnCr-LDH lamellar structure, and an articulated fiber structure of sepiolite was observed due to the large

Fig. 2. SEM images of the pure Sep, virgin LDH, and Sep@LDH composites.

amount of Sep. With decreasing Sep content, significant amounts of LDH particles were observed in the Sep₁@LDH, Sep₂@LDH, Sep₄@LDH, and Sep₆@LDH samples, where the Sep fibers appeared to be fully coated by the LDH lamella. Especially for the Sep₄@LDH sample, the SEM image showed a typical “sand-rose” morphology characteristic of hydrotalcite-like compounds with interconnected hexagonal lamellar plates almost uniform in size, which was consistent with the XRD results that showed Sep₄@LDH had the highest crystallinity of all samples. This indicated that a balanced amount of ZnCr-LDH coating on the surface of the Sep fibers caused a decrease in agglomeration of the composites.

3.1.3. N₂ adsorption-desorption isotherm analyses

To examine the textural characteristic of the prepared photocatalysts, BET gas sorptometry measurements were used to characterize their pore volume (V_p), pore diameter (D_p), and specific surface area (S_{BET}). The adsorption isotherms of the pure Sep, virgin LDH, and Sep@LDH composites are shown in Fig. 3. Except for Sep₄@LDH, all samples exhibited a typical H3 hysteresis loop in the high relative pressure (P/P_0) range of 0.60 to 0.97. The pure Sep and Sep₁₀@LDH exhibited similar adsorption isotherm curves with very small type H3 hysteresis loops from 0.80 to 0.97 (P/P_0) corresponding to a type II isotherm according to IUPAC classification, indicating the presence of tubular pores [15,31]. For the virgin LDH, Sep₁@LDH, and Sep₂@LDH, isotherms with typical H3 hysteresis loop in a relatively high pressure range of 0.70 to 0.97 (P/P_0) was observed due to aggregates of plate-like particles causing slit-like pores with nonuniform size and largely without micropores, belonging to typical type IV isotherms of mesoporous materials [2]. Only the Sep₆@LDH sample showed a hysteresis loop in the

Fig. 3. N₂ adsorption-desorption isotherms of the pure Sep, virgin LDH, and Sep@LDH composites.

Table 1

Textural parameters of the Sep@LDH composites.

Sample	S_{BET} (m ² ·g ⁻¹)	V_p (cm ³ ·g ⁻¹)	D_p (nm)
Sep	127	0.26	15.10
LDH	130	0.15	6.36
Sep ₁₀ @LDH	129	0.24	9.01
Sep ₆ @LDH	138	0.51	7.66
Sep ₄ @LDH	148	0.19	7.57
Sep ₂ @LDH	136	0.19	6.54
Sep ₁ @LDH	130	0.15	4.19

range of 0.60 to 0.97 (P/P_0) corresponding to a type IV isotherm, indicating the presence of pores formed by the parallel plates. Especially for the Sep₄@LDH sample, the isotherm with a hysteresis loop between type H3 and H4 was observed at a moderate relative pressure from 0.4 to 0.97 (P/P_0) corresponding to a type IV isotherm, indicating a broad pore size distribution and mesoporous structure. The pore formation was more likely caused by coverage of the LDH particles on the surface of the Sep fibers. As seen in Table 1, the corresponding surface areas (S_{BET}) of the samples suggested that the LDH coating with lamellar structure exerted a small impact on the S_{BET} of the Sep@LDH. The Sep₄@LDH composite showed the highest surface area (148 m²·g⁻¹), likely due to the presence of LDH with well-dispersed particles on the surface of the Sep fibers. These results indicated the mesoporous nature of Sep@LDH, and that appropriate coating of ZnCr-LDH on the surface of the Sep fibers caused an increase in the S_{BET} of the composites.

Fig. 4. TG-DTG patterns of the pure Sep, virgin LDH, and Sep@LDH composites.

3.1.4. TG/DTG analyses

The TG/DTG curves of the pure Sep, virgin LDH, and Sep@LDH composites are shown in Fig. 4. The pure Sep was heated in a multistep dehydration process from 25 to 700 °C. The weight loss was attributed to the removal of surface-adsorbed water, zeolite water, coordinated water, and hydroxyl groups. Another degradation step was observed due to the phase transformation of sepiolite to enstatite (MgSiO_3) at >700 °C, which was in good agreement with the literature [16,17]. For the virgin LDH, the thermal decomposition was evidenced by two well-differentiated peaks, which corresponded to the loss of surface and interlayer water (the first endothermic peak at 50–180 °C) and hydroxyl groups from the brucite sheets and the interlayer CO_3^{2-} anions for the second peak (180–400 °C) [18,19]. The TG and DTG curves of the Sep@LDH composites demonstrated similar pyrolysis behavior, where the endothermic step of the hydroxyl groups in the brucite sheets and interlayer CO_3^{2-} anions became gradually blurred with increasing coating amount of Sep. On the other hand, the total weight loss of the pure Sep was approximately 14.0 wt% at 700 °C, while the total weight loss of the virgin LDH was approximately 25.6 wt%. For the Sep@LDH composites, the total weight loss increased with increasing LDH, and the Sep₁@LDH exhibited the highest total weight loss of 25.2 wt%. Thus, it can be concluded that ZnCr-LDH was present in the Sep@LDH composites.

3.1.5. UV-Vis DRS analyses

UV-Vis DRS measurement is very simple, and can be used as a sensitive measure of changes in the molecular structure of materials. The UV-Vis DRS spectra of the pure Sep, virgin LDH, and Sep@LDH composites are shown in Fig. 5(A), where their band gaps were also estimated. The pure Sep exhibited a weak peak at 200–800 nm, while the virgin LDH showed three strong absorption bands at <320, 380–500, and 500–800 nm. This indicated that the ZnCr-LDH had strong absorption in the visible-light region due to the photoexcitation of the CrO_6 octahedron at approximately 430 nm and the $d-d$ transition of Cr^{3+} at approximately 600 nm [8,18]. Compared to the pure Sep, a new peak appeared at 600 nm for the Sep₁₀@LDH, which indicated the presence of Cr^{3+} . The Sep@LDH composites, except for Sep₁₀@LDH, exhibited a new peak at approximately 430 nm, indicating the presence of polymeric species with CrO_6 octahedral coordination. Moreover, the band gap transition of the composites was determined from the plots of $(\alpha h\nu)^2$ as a function of $(h\nu)$ based on the expression $(\alpha h\nu)^2 = A(h\nu - E_g)$ [20], and the related curves were plotted in Fig. 5(A) (inset). The band gap energies of the virgin LDH, Sep₁@LDH, Sep₂@LDH, Sep₄@LDH, and Sep₆@LDH were 2.30, 2.29, 2.27, 2.22, and 2.25 eV, respectively, suggesting that the virgin LDH and Sep@LDH composites showed potential for photocatalytic decomposition of MO and MB under visible light. It should be noted that the band-gap energies of the Sep@LDH composites were lower than that of virgin LDH, which can be attributed to the effect of the sepiolite carrier on the LDH crystal structure. Meanwhile, Sep₄@LDH exhibited the lowest band-gap energy among the prepared composites, suggesting that a balanced amount of the

Fig. 5. UV-Vis DRS (A) and PL (B) spectra of the pure Sep, virgin LDH, and Sep@LDH composites.

LDH increased the photoexcitation of the CrO_6 octahedron because of its high crystallinity and large surface area. The results were in good agreement with those of the XRD and SEM analyses.

3.1.6. PL analyses

PL spectra were measured to investigate the luminescence properties of the virgin LDH and Sep@LDH composites and are shown in Fig. 5(B). The main emission peaks for all samples were centered at approximately 350 nm corresponding to the band gap of ZnCr-LDH [21], and the PL spectra agreed well with the UV-Vis spectra. The emission can be attributed to band-band PL phenomena where the electron transitions from the CB bottom to VB top occurred. The emission of the band gap transition was equal to the band gap energy, consistent with previous research [22]. The highest PL emission intensity was observed for the Sep₁₀@LDH, due to its low amount of LDH coating. Stronger peak intensities of the Sep@LDH composites, except for that of Sep₄@LDH, were observed compared with that of the pure LDH. It should be noted that the Sep₄@LDH sample exhibited the largest extent of quenching. This phenomenon was attributed to its high crystallinity and dispersity, leading to many active sites on the surface of the Sep₄@LDH composite, enhancing electron-hole separation/transport [23]. The results suggested that a suitable LDH coating significantly

enhanced the electron-hole separation/transport, where the abundant electron-hole pairs (active sites) promoted carrier transport efficiency, leading to high photocatalytic activity towards the visible light-driven decomposition of MO and MB. This is further discussed in the following section.

3.2. Catalytic performance of the Sep@LDH composites

3.2.1. Catalytic activity

The photocatalytic activities of the composites were examined by monitoring the time-dependent degradation of MB and MO under visible-light irradiation ($\lambda > 420$ nm). As shown in Fig. 6, the adsorption of MB and MO on the samples contributed to their degradation. An MO adsorption ratio of 21.2% and MB adsorption ratio of 45.7% was observed for the pure Sep, while the MO and MB adsorption ratios were 40.4% and 20.7%, respectively, for virgin LDH after 30 min in the dark. When the LDH coating amount increased stepwise, the adsorption of MO gradually dropped, but the adsorption of MB increased on the Sep@LDH composites. On the other hand, it was clear that pure Sep showed little photocatalytic activity towards MO, while it exhibited weak catalytic activity towards MB (15.2% degradation ratio) under visible light after 120 min. However, after

Fig. 6. Adsorption and photocatalytic degradation of co-existing MO and MB in equal concentration (each $20 \text{ mg}\cdot\text{L}^{-1}$) with $1.0 \text{ g}\cdot\text{L}^{-1}$ catalyst loading.

coating with LDH, the Sep@LDH composites generally showed enhanced photocatalytic activity. Specifically, the Sep₄@LDH sample showed superior photocatalytic activities (removal ratios of 86.9% for MO and 81.5% for MB) under visible light after 120 min. In contrast, the virgin LDH only exhibited a removal ratio of 73.7% for MO and 61.8% for MB under the same conditions. The Sep₄@LDH composite exhibited the highest photocatalytic activity due to its large surface area, high crystallinity of the ZnCr-LDH formed on the surface of Sep, and low band-gap energy (2.22 eV). Thus, the appropriate LDH coating amount on the surface of Sep enhanced the photocatalytic activity, verifying the analytical UV-Vis DRS and PL results. To further optimize Sep₄@LDH, the experiments were performed by varying the catalyst loading from 0.25 to $2.0 \text{ g}\cdot\text{L}^{-1}$ (Fig. S5). The highest photocatalytic efficiency was observed at a loading of $1.25 \text{ g}\cdot\text{L}^{-1}$ Sep₄@LDH, which was selected to further evaluate the photocatalytic performance of the Sep₄@LDH composite. For practical application, the effect of the initial concentration of the dye substrates on the photocatalysis was also investigated, and the results are shown in Fig. 7. It was clearly demonstrated that the initial concentrations of MO and MB did not have a significant effect on the time required to reach equilibrium, and their removal ratios increased with decreasing initial concentrations. When the initial concentrations of MO and MB were $10 \text{ mg}\cdot\text{L}^{-1}$, the corresponding removal ratios were 99.0% and 93.3%, respectively, after 120 min.

Fig. 7. Photodegradation by the Sep₄@LDH ($1.25 \text{ g}\cdot\text{L}^{-1}$) catalyst at different initial concentrations of co-existing MO and MB in the dark for 30 min and subsequently under visible light for 120 min.

3.2.2. Reaction kinetics

To quantitatively understand the reaction mechanisms, the photocatalytic degradation of co-existing MB and MO was studied as a function of time over the Sep₄@LDH catalyst, and was found to follow the pseudo first-order kinetic model. The kinetics were well-described by the Langmuir-Hinshelwood (L-H model) which could accurately represent the experimental data of the photocatalytic reaction systems [24–26]. From the data obtained in this study (Fig. 7), the kinetic parameters were calculated according to the L-H model and are listed in Table 2. The calculated correlation coefficient (R^2) obtained from the model was higher than 0.96 ($R^2 > 0.96$), indicating that the L-H model was suitable for describing the photocatalytic reaction. As seen in Table 2, higher k values indicate better removal efficiency of the co-existing MO and MB under visible light, showing a similar trend where the catalytic activity increased with decreasing initial concentrations of MO and MB. To further investigate the reaction mechanism, the kinetic parameters of the photodegradation reaction over the virgin LDH and all Sep@LDH composites were calculated using the L-H model based on the data shown in Fig. 6 and Table S2. As seen in Table S2, the kinetic investigation confirmed that the photodegradation of MO and MB followed the L-H model for all studied catalysts ($R^2 > 0.95$). The results suggested that the active sites significantly influenced the rate of photodegradation, which verified the UV-Vis DRS and PL analyses. The classical L-H model was used under the hypothesis that the surface-active sites of the photocatalysts were energetically homogeneous [27] and confirmed that the moderate LDH coating on the surface of the Sep formed copious and homogeneous active sites leading to better photocatalytic activity.

3.2.3. Stability of the Sep₄@LDH catalyst

Catalyst recycling has often been problematic because of instability and leaching; therefore, a recycling experiment was performed. Each run was performed in the dark for 30 min, then exposed under visible light for 120 min, following which the Sep₄@LDH catalyst was reused for the next run under the same conditions. A total of five runs using the filtered catalyst were performed with washing to remove the reaction solution attached to the catalyst, and then drying at 80 °C for reuse (Fig. 8). Slight leaching of the active Cr species was detected, with Cr

Fig. 8. Stability and Cr leaching of the Sep₄@LDH (1.25 g·L⁻¹) in the degradation of co-existing MO and MB (10 mg·L⁻¹ each).

concentrations of 5×10^{-6} mol·L⁻¹ in the first cycle, 1×10^{-6} mol·L⁻¹ in second cycle, and no Cr detected after the third cycle. The catalytic activity (94.4% for MO and 90.2% for MB) declined mainly due to Cr leaching during the second cycle. In subsequent cycles, the catalyst was recycled without an obvious decrease in activity and was maintained at over 86.2% for MO and 84.9% for MB in the fifth cycle. These results suggested that the Sep₄@LDH catalyst has strong potential for good photocatalytic activity and stability.

3.2.4. Investigation of the photocatalytic reaction mechanism

To obtain further insight into the photocatalytic mechanism of Sep₄@LDH, the reactive oxygen species in the photocatalytic process were investigated by adding scavengers into the reaction system (Fig. 9). The formation of intermediate active species, such as superoxide anion radicals ($\bullet\text{O}_2^-$), hydroxyl radicals ($\bullet\text{OH}$), and photogenerated holes (h^+) during the photoreaction process, and their role, were indirectly investigated using three quenchers, *i.e.*, benzoquinone (BQ, an $\bullet\text{O}_2^-$ scavenger), disodium ethylenediaminetetraacetate (Na₂-EDTA, a h^+ scavenger), and tert-butanol (*t*-BuOH, an $\bullet\text{OH}$ scavenger) [28,29]. Upon introducing *t*-BuOH, the photocatalytic activity was almost completely quenched, implying that hydroxyl radicals ($\bullet\text{OH}$) were the dominant reactive species contributing to the photodegradation of co-existing MO and MB. When Na₂-EDTA was added, the h^+ holes were scavenged, but $\bullet\text{OH}$ could still participate in the photo-degradation process, so the photocatalysis was only partially suppressed. With the addition of BQ, most of the MO and MB were degraded, indicating that $\bullet\text{O}_2^-$ radicals played a very minor role in the photocatalytic degradation. Based on the above results, a photodegradation mechanism of co-existing MO and MB by the Sep₄@LDH composite under visible-light irradiation was proposed as follows,

Table 2

Kinetic parameters for the degradation of co-existing MO and MB.

Substrate	C_0 (mg·L ⁻¹)	η (%)	L-H model $\ln(C_0/C_t) = kt$ [24–26]		
			k_1 (L·mg ⁻¹ ·min ⁻¹)	r_1^2	$t_{1/2}$ (min)
MO	10	98.96	0.0190	0.9904	37
	20	93.75	0.0133	0.9825	52
	25	64.58	0.0048	0.9748	144
	30	53.66	0.0032	0.9755	217
	10	93.12	0.0114	0.9759	60
MB	20	87.32	0.0111	0.9713	62
	25	56.72	0.0044	0.9642	158
	30	49.61	0.0036	0.9614	193

Where η is the removal ratio (%), C_0 is the initial concentration of MO (or MB), C_t is the concentration (mg·L⁻¹) at time t (min), and k is the rate constant of the L-H model.

Fig. 9. Photodegradation of mixed MO and MB ($10 \text{ mg} \cdot \text{L}^{-1}$ each) by $\text{Sep}_4\text{@LDH}$ ($1.25 \text{ g} \cdot \text{L}^{-1}$) with different scavengers ($1.0 \text{ mmol} \cdot \text{L}^{-1}$) in the dark for 30 min and subsequently under visible light for 120 min.

Scheme 2. Photocatalysis on the ZnCr/LDH under visible-light irradiation.

form $\bullet\text{OH}$ radicals which degraded the dyes (MO and MB). The e^- -absorbed dioxygen on the surface of the catalyst produced $\bullet\text{O}_2^-$ radicals, which were then reduced to $\bullet\text{OH}$ via disproportionation of $\bullet\text{O}_2^-$ [30]. Lastly, the MO and MB molecules were oxidized and decomposed by the $\bullet\text{OH}$ radicals. Therefore, according to these findings, it can be concluded that $\bullet\text{OH}$ radicals played a critical role in the photocatalytic degradation process of co-existing MO and MB by the Sep@LDH composites (Scheme 2).

4. Conclusions

Sep@LDH composites were successfully synthesized by a facile *in situ* co-precipitation method and showed photocatalytic activities toward the degradation of co-existing MO and MB under visible light, where the acid-activated Sep was as an excellent carrier. The composites were characterized by XRD, SEM, BET/BJH, TG/DTG, UV-Vis DRS, and PL methods, indicating that ZnCr-LDH was coated on the Sep surface successfully. A moderate amount of coating of the ZnCr-LDH generated a good distribution of the Sep@LDH particles with high crystallinity and large surface area, which increased the number of active sites on the surface of Sep@LDH resulting in high photocatalytic activity. Among the Sep@LDH composites, $\text{Sep}_4\text{@LDH}$ exhibited the best photocatalytic performance. In addition, the degradation kinetics were fitted to a pseudo first-order kinetic model, which confirmed that the active sites were a crucial factor in the photodegradation. The good degradation of the dye pollutants was attributed to the generation of highly oxidative $\bullet\text{OH}$ radicals at the active sites and electron/hole pairs during the photodegradation reaction.

References

- [1] Y. Zhang, D. Wang, G. Zhang, *Chem. Eng. J.*, **2011**, 173, 1–10.
- [2] J. Han, Y. H. Zeng, S. Xu, R. C. Chen, J. X. Liu, *Appl. Catal. A*, **2016**, 527, 72–80.
- [3] M. Doğan, Y. Özdemir, M. Alkan, *Dyes Pigments*, **2007**, 75, 701–713.
- [4] L. Mohapatra, K. Parida, M. Satpathy, *J. phys. Chem. C*, **2012**, 116, 13063–13070.
- [5] L. J. Gunjkar, Y. I. Kim, M. J. Lee, S. N. Lee, J. S. Hwang, *Energy. Environ. Sci.*, **2013**, 6, 1008–1017.
- [6] J. S. Xia, X. F. Liu, M. Z. Ni, L. J. Xue, P. P. Qian, *J. Colloid. Interf. Sci.*, **2013**, 405, 195–200.
- [7] Š. Paušová, J. Krýsa, J. Jirkovský, C. Forano, G. Mailho, V. Prevot, *Appl. Catal. B*, **2015**, 170, 25–33.
- [8] L. Mohapatra, M. K. Parida, *Sep. Purif. Technol.*, **2012**, 91, 73–80.
- [9] Q. Liu, J. Ma, K. Wang, T. Feng, M. Peng, Z. Yao, S. Komarneni, *Ceram. Int.*, **2017**, 43, 5751–5758.
- [10] A. Özcan, S. A. Özcan, *J. Hazard. Mater.*, **2005**, 125, 252–259.
- [11] Y. Gao, H. Gan, G. Zhang, Y. Guo, *Chem. Eng. J.*, **2013**, 217, 221–230.
- [12] G. Zhang, Q. Xiong, W. Xu, S. Guo, *Appl. Clay Sci.*, **2014**, 102, 231–237.
- [13] M. Akkari, P. Aranda, A. Mayoral, M. García-Hernández, A. Ben Haj Amara, E. Ruiz-Hitzky, *J. Hazard. Mater.*, **2017**, 340, 281–290.
- [14] F. Cavani, F. Trifirò, A. Vaccari, *Catal. Today*, **1991**, 11, 173–301.
- [15] M. Suárez, E. García-Romero, *Appl. Clay Sci.*, **2012**, 67, 72–82.
- [16] N. A. Ökte, E. Sayinsöz, *Sep. Purif. Technol.*, **2008**, 62, 535–543.

Graphical Abstract

Chin. J. Catal., 2018, 39: 1832–1841 doi: 10.1016/S1872-2067(18)63120-1

Facile preparation of sepiolite@LDH composites for the visible-light degradation of organic dyes

Li Jin, Hong-Yan Zeng*, Sheng Xu, Chao-Rong Chen, Heng-Zhi Duan, Jin-Ze Du, Guo Hu, Yun-Xin Sun
Xiangtan University

Sep@LDH composites were successfully synthesized by a facile *in situ* co-precipitation method and exhibited high photocatalytic performances towards the degradation of co-existing MO and MB under visible-light irradiation, where Sep was an excellent carrier.

- [17] G. Tartaglione, D. Tabuani, G. Camino, *Microporous Mesoporous Mater.*, **2008**, 107, 161–168.
- [18] K. Parida, L. Mohapatra, *Dalton Trans.*, **2012**, 41, 1173–1178.
- [19] P. Koilraj, S. Kannan, *Chem. Eng. J.*, **2013**, 234, 406–415.
- [20] F. Liu, Y. Lai, J. Liu, B. Wang, S. Kuang, Z. Zhang, Y. Liu, *J. Alloy. Compd.*, **2010**, 493, 305–308.
- [21] C. Wang, B. Ma, S. Xu, D. Li, S. He, Y. Zhao, J. Han, M. Wei, D. G. Evans, X. Duan, *Nano Energy*, **2017**, 32, 463–469.
- [22] N. Baliarsingh, L. Mohapatra, K. Parida, *J. Mater. Chem. A*, **2013**, 1, 4236–4243.
- [23] Y. Hou, B. A. Laursen, J. Zhang, G. Zhang, Y. Zhu, X. Wang, S. Dahl, I. Chorkendorff, *Angew. Chem. Int. Ed.*, **2013**, 52, 3621–3625.
- [24] T. C. Hsieh, S. W. Fan, Y. W. Chen, Y. J. Lin, *Sep. Purif. Technol.*, **2009**, 67, 312–318.
- [25] D. Chen, Y. Li, J. Zhang, Z. J. Zhou, Y. Guo, H. Liu, *Chem. Eng. J.*, **2012**, 185, 120–126.
- [26] N. Baliarsingh, M. K. Parida, C. G. Pradhan, *Ind. Eng. Chem. Res.*, **2014**, 53, 3834–3841.
- [27] S. Armenise, E. Garcia-Bordeje, L. J. Valverde, E. Romeo, A. Monzón, *Phys. Chem. Chem. Phys.*, **2013**, 15, 12104–12117.
- [28] J. Jiang, H. Li, L. Zhang, *Chem. Eur. J.*, **2012**, 18, 6360–6369.
- [29] J. Tang, Y. Liu, H. Li, Z. Tan, D. Li, *Chem. Commun.*, **2013**, 49, 5498–5500.
- [30] C. Zhao, M. Pelaez, D. D. Dionysiou, C. S. Pillai, A. J. Byrne, E. K. O'Shea, *Catal. Today*, **2014**, 224, 70–76.
- [31] Y. Li, K. Lv, W. Ho, Z. Zhao, Y. Huang, *Chin. J. Catal.*, **2017**, 38, 321–329.
- [32] W. Lin, H. Cheng, X. Li, C. Zhang, F. Zhao, M. Arai, *Chin. J. Catal.*, **2018**, 39, 988–996.

水滑石与海泡石复合材料对有机染料的光催化降解性能

金力, 曾虹燕*, 徐圣, 陈超容, 段恒志, 杜金泽, 胡果, 孙云鑫
湘潭大学化工学院, 湖南湘潭411105

摘要: 由于ZnCr-LDH纳米粒子具有良好的光催化性能, 但极易团聚, 在一定程度上制约了它在光催化领域的应用. 将水滑石制成核-壳复合材料可以避免粒子团聚, 改善其单分散性和稳定性, 从而提高光催化活性. 本文设计了一种水滑石/海泡石(Sep@LDH)纳米复合材料作为光催化剂, 以甲基橙(MO)和亚甲基蓝(MB)混合溶液模拟有机染料废水, 进行光催化反应. 通过XRD, SEM, UV-Vis DRS, PL, TG-DTG和BET/BJH, 证明了水滑石成功的生长在海泡石的表面, 通过光催化实验详细研究了Sep@LDH纳米复合材料的光催化性能及光降解反应机理.

采用共沉淀制备了不同Zn/Cr摩尔比的水滑石纳米材料, 对水滑石进行优化, 结合表征分析, 发现摩尔比为1的ZnCr-LDH其结晶度、层间规整度高, 禁带宽度最窄(2.30 eV)和光致发光性能最佳. 因而用作后续复合材料的制备.

另一方面, 我们以酸活化的海泡石(Sep)为载体, 采用原位生长法成功制备了一种新型的水滑石/海泡石(Sep@LDH)光

催化剂,研究了海泡石的添加量对复合材料性能的影响.结果表明, Sep含量对复合材料形貌、粒径大小、结构以及光学性质影响较大.其中,样品Sep₄@LDH (海泡石添加量为4 g),比表面积最大,因而光催化效率最高.降解动力学结果表明,染料的光降解过程遵循准一级动力学模型.

我们通过对活性物种($\bullet\text{OH}$, h^+ , $\bullet\text{O}_2^-$)的考察,研究了光催化降解机理.结果表明, $\bullet\text{OH}$ 在光降解过程中起着至关重要的作用. Sep₄@LDH复合材料循环使用5次后, MO和MB的光降解率依然分别可以达到86.2%和84.9%,表现出较高的稳定性.

关键词: 水滑石; 海泡石; 光催化性能; 水处理; 纳米材料

收稿日期: 2018-04-15. 接受日期: 2018-06-04. 出版日期: 2018-11-05.

*通讯联系人. 电话: (0731)58298175; 电子信箱: hongyangezeng99@hotmail.com, hyzeng@xtu.edu.cn

基金来源: 湖南省自然科学基金会(湘潭市)联合研究项目(2016JJ5030); 湖南省2011年化学工程技术协同创新中心与湖南省教育厅环境效益和资源有效利用合作项目(17C1526); 湘潭大学博士创业基金(17QDZ05); 湘潭大学本科创新实验项目(2017XJ067).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).