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Nano-TiO$_2$ immobilized on diatomite: characterization and photocatalytic reactivity for Cu^{2+} removal from aqueous solution

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Abstract

Using the diatomite as the carrier, the nano-TiO$_2$/diatomite composite materials (NTID) were synthesized by the hydrolysis deposition of titanium tetrachloride. Thermodynamic behavior of the as-prepared sample was evaluated by thermo gravimetric (TG) and differential scanning calorimetry (DSC). Structures of the composite were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS). The photocatalytic property of the composite was investigated through the degradation of Cu^{2+} in aqueous solutions. Effects of various parameters such as initial pH, catalyst amount and initial Cu^{2+} concentration on the removal of Cu^{2+} were investigated to optimize operational conditions. The results indicate that the nano-TiO$_2$ immobilized on the surface of carrier was crystallized through calcinations at 700 °C. And the phase of TiO$_2$ is anatase with the average crystallite size of 13 nm. The removal efficiency of 10 mg/L Cu^{2+} solution by the composite reaches 96.63% after irradiation for 3 h under UV-light.

1. Introduction

As the accelerated process of industrialization and the development of urbanization, statistical analysis revealed that industrial wastewater discharge, which consists of excessive heavy metal irons, was found increasing annually [1]. Due to the high toxicity of heavy metal irons, pollution of water with these species has lead to challenges for the

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environmental protection even at a low concentration [2]. Cu^{2+} is one of common heavy metals in wastewater originated from the effluents of electroplating, electrical industry, wire mills and other industrial plants [3, 4]. Cu^{2+} in wastewater will be enriched through the food chain and the accumulation of Cu^{2+} in human body causes mucosal irritation, widespread capillary damage, hepatic and renal damage [5, 6]. Over the past decade, numerous treatment technologies have proposed to remove Cu^{2+}, such as activated carbon adsorption, chemical reduction, biological degradation and ion exchange [7, 8]. Compared with traditional methods, photocatalytic reduction of Cu^{2+} by semiconductor materials has attracted wide attention. Because photocatalysis is an environmentally friendly process and it can avoid causing secondary pollution [9, 10].

Recently, TiO_2 which is one of the common photocatalysts has been the most widely investigated due to its low cost, chemical stable and high efficiency properties [11]. Heavy metal irons pollutants such as Hg^{2+}, Cu^{2+}, Ni^{2+} and Cr^{6+} have been successfully degraded by illuminated TiO_2 under ultraviolet light [12-14]. Nanotechnology is thus expected to improve the performance of TiO_2 for water treatment. However, TiO_2 nanoparticles are easy to aggregate and difficult to recovery in aqueous solution during practical application [15, 16]. Materials like activated carbon [17], zeolite [18], kaolinite [19] and montmorillonite [20] have been investigated to load TiO_2 particles to avoid these difficulties. The porous materials are involved the adsorption of pollutants on the surface sites, then the photocatalytic degradation of pollutants is improved, simultaneously [21]. Diatomite (DIA) which consists of amorphous silica ($SiO_2 \cdot nH_2O$) has a large specific surface area, a specific porous structure and strong sorption ability, resulting in an attractive force toward heavy metals [22, 23].

In this study, the nano-TiO_2 was immobilized on diatomite by a typical hydrolysis deposition method. And the structures of the as-prepared samples were characterized by TG-DSC, XRD, SEM and EDS. The photocatalytic activity of diatomite-based nano-TiO_2 for Cu^{2+} removal from aqueous solution was evaluated by investigating the effects of various conditions.

2. Experiment

2.1. Reagents and samples preparation

Diatomite was obtained from Linjiang (Jilin province, China) and acid leached to remove impurities. The stock solution of 1000mg/L Cu^{2+} was made by dissolving certain weight dried $Cu(NO_3)_2$ in distilled water. All the Cu^{2+} solution with required concentrations were diluted from the stock solution. The pH of solution was adjusted by dilute NaOH and HNO_3 solution and monitored by a pH meter (FE20, Mettler-Toledo Instruments Co., Ltd.). All reagents used in this work were of analytical grade and distilled water was used. Nano-TiO_2 was immobilized on diatomite by a hydrolysis deposition method which has been described by our research group before [24, 25]. In the typical synthesis, 10g diatomite was dispersed in 300ml water in an ice-water bath. Subsequently, 2ml HCl was added into the suspension. And then an amount of $TiCl_4$ aqueous solution and $(NH_4)_2SO_4$ were added with a speed of 100mL/h and the molar ratio of $TiCl_4$: $(NH_4)_2SO_4$ was maintained at 1:1 during the reaction. After that $NH_3 \cdot H_2O$ was used to adjust pH to 6 for the hydrolysis precipitation reaction at 40 °C. The resulting suspension was stirred for 1h, filtrated and washed for several times and then dried at 100 °C overnight.

2.2. Experimental system

Photocatalytic experiments were carried out in quartz tubes with a volume of 150 ml as shown in Fig. 1. Each tube containing the sample and 100ml Cu^{2+} solution was exposed to ultraviolet radiation from a 200W high pressure Hg lamp. The distance between the Hg lamp and the tube was kept approximately 10 cm. the Cu^{2+} solution and catalysts in the reactor were constantly stirred by a magnetic stirrer. Formic acid was used as a hole scavenger to prevent the recombination of electron–hole pairs in the photocatalytic experiments and the concentration of formic acid was 5 mmol/L [26, 27]. For reference, the adsorption of Cu^{2+} by the samples in the absence of UV irradiation was studied in similar conditions. At different time intervals, samples of 4 ml solution were taken out. After samples collection, catalyst was removed by centrifugation at 3500r/min, and then filtered by 0.45 μm membrane filter. Then, the concentration of the Cu^{2+} ions in the aqueous phase was analyzed by spectrophotometer method with oxalic acid

bis-cyclohexylidene hydrazide by using a UV-visible spectrophotometer (UV-9000, Shanghai Metash), Germany) [28].
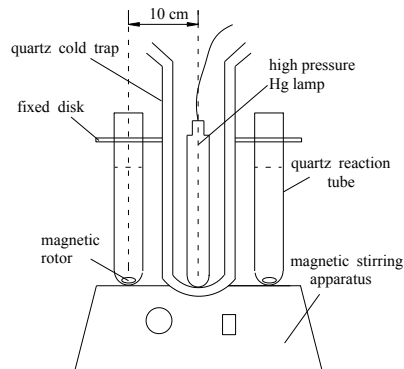

Fig. 1. The schematic diagram of photocatalytic reactor.

The degradation efficiency of Cu^{2+} is defined as follows:

$$\eta = \frac{C_0 - C}{C_0} \times 100\%$$

(1)

Where η is the degradation efficiency of Cu^{2+}; C_0 is the initial concentration of Cu^{2+} (mg/L); C is the concentration of Cu^{2+} at reaction time t (mg/L).

2.3. Characterization

Thermo gravimetric (TG) and differential scanning calorimetry (DSC) were performed using a METTLER 1/1600HT thermo gravimetric analyzer (Switzerland) under atmosphere at a heating rate of 10°C/min. X-ray diffraction (XRD) analysis was carried out on a Bruker D8 ADVANCE X-ray diffractometer (Germany) with Cu-Kα radiation (λ=1.54178 Å), which was operated at 40kV and at 40mA. The scanning electron microscopy (SEM) was recorded on a Hitachi S-4800 filed emission gun-scanning electron microscope (Japan) with an energy dispersive spectrometer for microanalysis.

3. Results and discussion

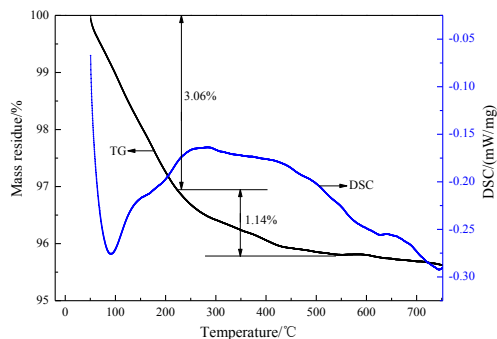### 3.1. Characteristics of samples

Fig. 2 The TG-DSC curves of NTID.

Thermo gravimetric and differential scanning calorimetry curves of as-prepared samples during the course of calcinations in air are shown in Fig. 2. According to TG analysis, a large number weight loss, 3.06%, is observed from room temperature to 220 °C due to the remove of physically adsorbed water molecules and organic residue in sample. And there is an obvious endothermic peak at around 95 °C in DSC curve accompanying with the weight loss. The first exothermic peak is around 285 °C, then the relative wide and broad exothermic peak has been extended to 600 °C relates to decomposition of $Ti(OH)_4$ and slow formation of anatase TiO_2. In the temperature range of 220-600 °C, the mass loss is about 1.14%. Above 600 °C, no significant weight loss is observed, which indicates that the amorphous hydrated TiO_2 has transformed into crystalline TiO_2 through calcination. So the final power of nano-TiO_2-DIA composite (NTID) for photocatalytic reaction was obtained though calcination with a heating rate of 10 °C/min at 700 °C for 2h.
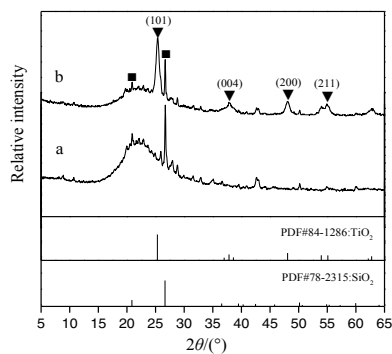

Fig. 3 XRD patterns of DIA and NTID.

For structure and phase analysis, X-ray diffraction analysis was employed and the XRD patterns of DIA and NTID are shown in Fig. 3(a) and Fig. 3(b), respectively. The diffraction spectrum of DIA only exhibits diffraction peaks of SiO_2 at 2θ of 20.86° and 26.64°, while there are four additional peaks in patterns of NTID, corresponding to diffraction peaks of TiO_2. The average crystalline size of TiO_2 nanoparticles in NTID, which is calculated from the FWHM (full-width at half-maximum) of diffraction peaks using Scherrer formula, is 13 nm. And the TiO_2 was 100% in crystal of anatase phase.
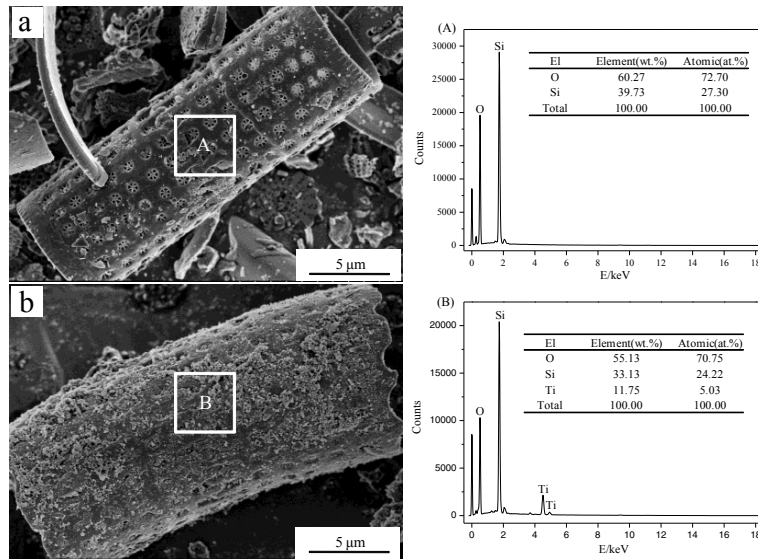
Fig. 4 SEM figures of DIA (a) and NTID (b) and EDS spectrum results.

The SEM images of DIA and NTID are shown in Fig. 4(a) and Fig. 4(b), respectively. From Fig. 4(a), it was found that the pore structures were uniformly distributed on the surface of DIA, which is in favour of high adsorption capacity for Cu^{2+}. After the TiO_2 immobilized on DIA, TiO_2 particles which distributed on the surface of NTID was help to improve the photocatalytic activity. Electron dispersive X-ray spectrometer (EDS) was used to confirm the composition of samples and the results of surface area analysis shown in Fig. 4(A) and Fig. 4(B), respectively. The characteristic peaks for Si, O can be observed in Fig. 4(A), which means that the main component of DIA is SiO_2. Compared with the EDS spectrum of DIA, the characteristic peaks for Ti were also observed in NTID which is consistent with the results obtained from XRD experiment and the content of Ti is 11.75 wt%.
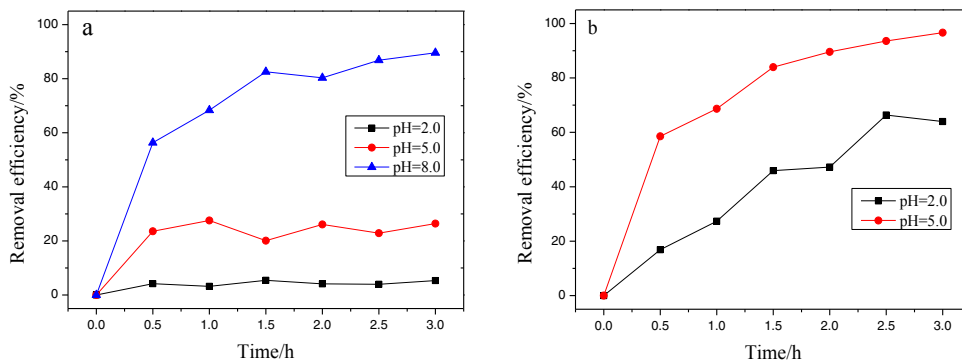
3.2. Effect of solution pH

Fig. 5 Effects of initial pH on the Cu^{2+} removal by NTID in dark (a) and under UV illumination (b) ($C_0(Cu^{2+})$ =10 mg/L, catalyst amount=2 g/L)

The optimal pH values for the removal of Cu^{2+} by NTID were investigated in different initial solution pH of 2.0, 5.0, and 8.0, respectively (Fig. 5). As is shown in Fig. 5(a), the adsorption was an important process for the removal

of Cu^{2+} in dark and the removal efficiency increased as the solution pH increased in the initial pH range 2.0-5.0. In the initial pH of 8.0, where the removal of the Cu^{2+} was almost 90%, overmuch OH^- may be attribute to the deposition of $Cu(OH)_2$, which may increase the amount of adsorption. To avoid Cu^{2+} precipitation at pH >8.0, and to invest the removal efficiency of Cu^{2+} from solution by the adsorption and degradation process, initial solution pH $\leqslant 5.0$ was chosen as the experimental conditions. So the case of the experimental solution pH >8.0 was without further considered. The effects of pH on the removal efficiency of Cu^{2+} under UV illumination were invested keeping all other factors constant. The results are reported in Fig. 6(b). It was observed that the higher the initial pH of solution, the greater was the efficiency of Cu^{2+} removed with the same trends as adsorption experiment. According to these results, it may be explained that the adsorption of Cu^{2+} has a promotion responsible for photocatalytic process. And the pH of 5.0 is chosen as the optimum value for further experiment to avoid the occurrence of $Cu(OH)_2$ prediction.
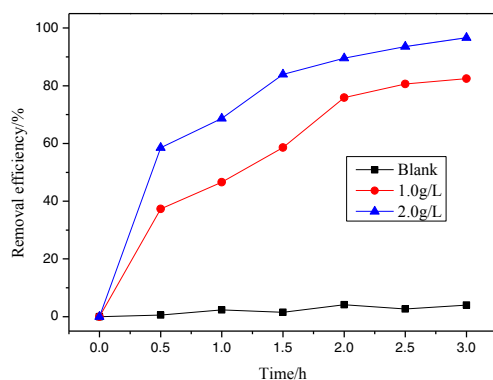
3.3. Effect of amount of catalyst

Fig. 6 Effect of amount of catalyst on the Cu^{2+} removal by NTID under UV illumination ($C_0(Cu^{2+})$=10 mg/L, pH=5.0)

The effect of catalyst amount on the Cu^{2+} removal was investigated by varying the initial catalyst dosage (0, 1, 2 g/L) at initial concentration of 10 mg/L. And the results were shown in Fig. 6. It was observed that the removal of Cu^{2+} without of catalyst was almost negligible. When the amount of catalyst was 1 and 2 g/L, it was found that the NTIF exhibited significant photocatalytic activity for the degradation of Cu^{2+}. The removal efficiency of Cu^{2+} increases as the catalyst dosage increased. This trend can be explained by increasing the reaction sites.

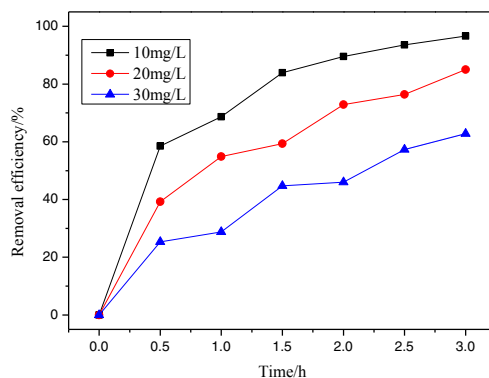### 3.4. Effect of Cu^{2+} concentration

Fig. 7 Effect of concentration on the Cu^{2+} removal by NTID under UV illumination (catalyst amount=2 g/L, pH=5.0)

The removal of Cu^{2+} by NTID under UV irradiation was investigated with the variation of initial Cu^{2+} concentration (10, 15 and 20 mg/L) at initial pH of 5.0 and at constant NTID amount (2 g/L). Fig. 7 shows that the removal efficiency of Cu^{2+} decreased as the initial Cu^{2+} concentration increased. The possible reason is that when the initial Cu^{2+} concentration increased, more Cu^{2+} can be removed on the surface of NTID. Large amount of cooper which may precipitate on the surface of NTID has an inhibitive effect on the further photocatalytic reaction of Cu^{2+}.

3.5. Kinetics

In order to obtain the kinetic mechanism during the photocatalitic process, the experimental results in Fig. 7 were fitted with the pseudo first-order model which is commonly expressed as the following equation [29]:

$$\ln\left(C/C_0\right) = -k_{\text{obs}} \cdot t \tag{2}$$

Where C_0 and C are the Cu^{2+} concentrations at initial stage and at time of t, respectively and k_{obs} is the observed rate constant of the pseudo ficrst-order reaction (h^{-1}) and t is the reaction time.
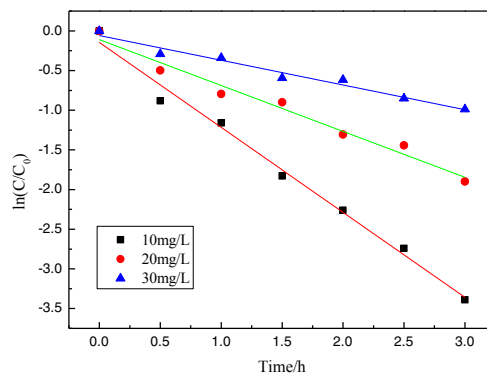
Fig. 8 Kinetic curves of for the Cu^{2+} removal by NTID under UV illumination

The plots of $\ln[(Cu^{2+})_t/(Cu^{2+})_0]$ versus time produced linear lines (see Fig. 8) with the value of correlation coefficients $R^2 > 0.95$, indicating that the rate of Cu^{2+} removal fitted well with this model.

3.6. Photocatalytic degradation mechanism of Cu^{2+}

To better understand the photocatalytic degradation mechanism of Cu^{2+}, photocatalytic reduction of Cu^{2+} which has been previously reported mechanisms of Cu^{2+} photocatalytic degradation by TiO_2 can be possible through the following mechanisms [30, 31]:
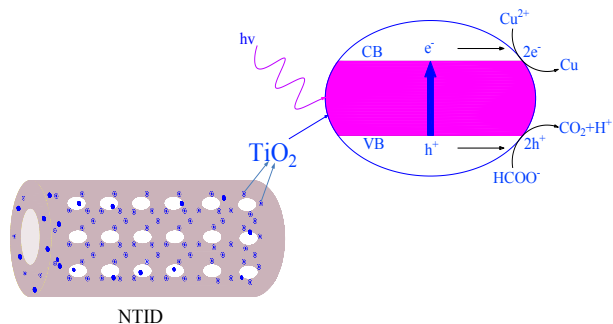
Fig. 9 The schematic diagram of mechanism for the photodegradation of Cu^{2+} by NTID.

Under the UV irradiation, electron (e^-) and hole (h^+) pairs are generated on surface of nano-TiO_2. The Cu^{2+} when is adsorbed in the NTID will be reduced into Cu by e^-. And the role of formic acid, as hole scavenge, promoted the photocatalytic reaction simultaneously. The H^+ produced through the reaction also needs a higher of the solution pH which corresponding to the photocatalytic degradation in section 3.2.

4. Conclusion

Nano-TiO_2 immobilized on diatomite was successfully prepared in this study and TiO_2 particles can be well crystallized on the surface of diatomite through calcinations at 700 for 2h. The phase of nano-TiO_2 is anatase and the average crystallite size is 13 nm. The results which obtained in dark evidenced that adsorption of Cu^{2+} on the NTID are strongly dependent on the solution pH. And the adsorption has a correlation with the efficiency of photocatalytic reaction. The photocatalytic removal of Cu^{2+} was investigated on the influence of parameters such as pH, amount of catalyst and concentration. The best removal is achieved at an optimal amount of 2 g/L and pH of 5.0. The removal efficiency of 10 mg/L Cu^{2+} solution by NTID reaches 96.63% after irradiation for 3 h. Under the optimized conditions, the removal of Cu^{2+} followed a pseudo-first order kinetic model.

Acknowledgements

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