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Photocatalytic reduction of phosphorus in the acid pickling milling wastewater from high-phosphorus hematite mineral processing

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ABSTRACT

The photocatalytic reduction of phosphorus in the acid pickling milling wastewater from high-phosphorus hematite mineral processing was innovatively performed in the absence of oxygen and in the presence of hole scavenger under visible light irradiation with Sr-doped TiO_2 in the study. Types and ratio of hole scavenger, effect of reduction time, dosage of Sr-doped TiO_2 and initial phosphorus concentration on the reduction of phosphorus were investigated. Experimental results indicated that the gaseous product of the photocatalytic reduction was identified to be phosphine. The optimum amount of formic acid and TiO_2 were 60 mmol l^{-1} and 2.0 g l^{-1}, respectively, and the phosphorus removal could reach 99.96% when used to treat the actual mineral processing wastewater. The photocatalytic reduction of phosphorus could be described by first order kinetic equation, and the reaction rate was proportional to the concentration of reactants.

Keywords: Photocatalytic reduction; Phosphorus; Titanium dioxide; Visible light; Doping; Formic acid;

1. Introduction

The hematite with high amounts of phosphorus is one of the most important iron minerals distributed broadly in nature. The acid pickling milling wastewater from hematite mineral processing was beneficiation wastewater with high phosphorus concentration produced in iron ore mineral processing technology. In recent decades, a large volume of the acidic wastewater containing phosphorus discharged directly into environment has caused serious water pollution [1,2]. In order to respond to the demand for removing excessive phosphorus from water, many technologies for phosphorus and other harmful wastes removing have been developed. The current technologies include physical chemical methods, biological methods and photochemistry methods [3–9]. Among them, physical chemical method is widely used for phosphorus removal but its cost and sludge production makes the treatment an unattractive option for wastewater treatments. The biological method is low-cost but the variability in chemical composition and temperature of wastewater would make the implementation of this process not feasible for wastewater treatment [10,11].

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Recently, a variety of photocatalytic processes have been studied for treating wastewater [12–15], while few documents about photocatalytic reduction of phosphorus have been reported so far.

Among the photocatalysts studied, titanium dioxide (TiO_2) has been considered as one of the most practical candidates owing to its low toxicity, high stability and prominent catalytic efficiency [16–19]. From the viewpoint of practical applications, however, the large band gap of TiO_2 is recognized to be the major disadvantage of powdered TiO_2. As a consequence, TiO_2 shows photocatalytic activities only in the near-ultraviolet (UV) region and responding to only a small fraction of visible light [20–22], limiting its range of application. The photocatalytic reaction may be drastically promoted by doping TiO_2 with a certain kind of metal. Numerous reports have been published on the photocatalytic activities that were enhanced the treatment effect of wastewater by platinum-and/ruthenium-or other metal-doped TiO_2 photocatalysts [23–26].

Strontium is an alkaline earth metal group element, and widely distributed in nature of trace elements, so strontium ion was selected as a TiO_2 modifier to investigate its properties in this paper. Sr-doped TiO_2 was prepared by the sol-gel methods. And its photocatalytic activities were evaluated by measuring photocatalytic reduction effect of phosphorus in the acid pickling milling wastewater from high-phosphorus hematite mineral processing under visible light irradiation.

2. Experimental

2.1. Materials and reagents

The acid pickling milling wastewater from high-phosphorus hematite mineral processing tested in the experiment was taken from Enshi Chaoyang Iron Ore, Hubei province, China. The total phosphorus (TP) concentration (existence form PO_4^{3-}–P) was 63.4 mg l^{-1}, and the pH value was 2.53, and the main metal ions in the wastewater were shown in Table 1.

The analytical reagents used in the experiment are as follows: tetrabutyl titanate, polyethylene glycol, glacial acetic acid, absolute ethyl alcohol, monopotassium, formic acid, methanol, acetic acid, alcohol, oxalic acid and sodium oxalate. The test water was deionized water made in the laboratory. A 125 W high-pressure mercury lamp (GYZ 220-125W, JingShuo lighting company, China), the effective range of the light spectrum between 350 and 450 nm, the main peak 365 nm, luminous flux 1500 Lm, which mainly emits a visible light, was used as a light source of the photocatalytic reduction.

Table 1
Metal ions in the wastewater (mg l^{-1})

Metal ion	Al	Ca	Fe	Mg	Zn	Si
Concentration	296.20	1743.30	167.15	92.00	6.63	100.15

2.2. Preparation of Sr^{2+}-doped TiO_2 powder

TiO_2 was prepared using a sol-gel method and the TiO_2 sol was obtained using tetrabutyl titanate as precursor. The proportion of tetrabutyl titanate, polyethylene glycol, deionized water, glacial acetic acid was 30:3:5:15. Sixty millilitres $Ti(OBu)_4$ was dissolved in 120 ml absolute ethyl alcohol with electromagnetic stirring for 1 h; then the solution containing 10 ml deionized water, 30 ml glacial acetic acid, 6 ml polyethylene glycol and 0.2 g strontium chloride was dropwise added to the above solution under stirring for 1 h, and then the transparent yellow sol was dried for 15 min at 100°C. At last the Sr^{2+}-doped TiO_2 powder of which the Sr/TiO_2 ratio was 0.09% (wt) was obtained after being calcined in the microcomputer control temperature system to achieve the crystal transforming. (The preliminary experiment has showed that the optimal Sr/TiO_2 ratio was 0.09% under the consideration of both treatment effect and cost, so 0.09% was chosen as the Sr/TiO_2 ratio in the study.)

2.3. Photocatalytic reduction experiment

The photoreactor system was shown in Fig. 1. It consisted of a quartz beaker reactor with the volume of 250 ml, a magnetic stirring apparatus, a 125 W high-pressure mercury lamp and a nitrogen pump.

The photocatalytic reduction activities of Sr^{2+}–TiO_2 were tested by measuring the removal of phosphorus in the acid pickling milling wastewater from high-phosphorus hematite mineral processing. A certain amount of photocatalysts were immersed into 100 ml acid pickling milling wastewater with phosphorus

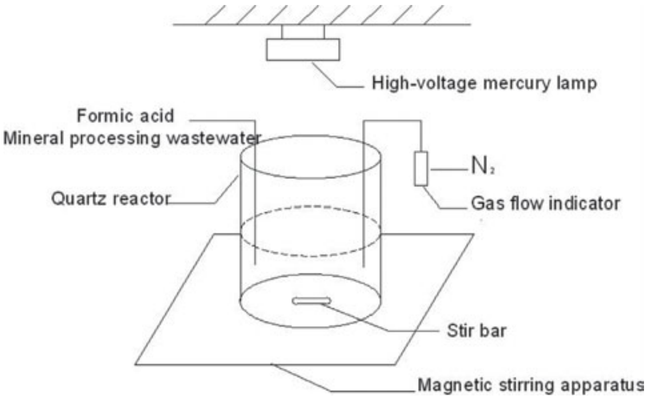

Fig. 1. Sketch of photoreactor.

concentration 63.4 mg l^{-1}. The suspension on the magnetic stirring apparatus was constantly stirred with stir bar under the continuous stream of nitrogen with a velocity of 0.1 l^{-1} min during the reaction. It was irradiated under the high-pressure mercury lamp (125 W) and added hole-trapping dopant after being purged with nitrogen for 0.5 h. The visible light was irradiated perpendicularly to the solution and the distance between the high-pressure mercury lamp and the liquid level was 30 cm. At given irradiation time intervals, liquid samples were taken from the suspension and treated with centrifugal separation, filtered with 0.2 μm membrane filter to remove TiO_2 particles, then the phosphorus in the filtrate was measured.

2.4. Analytical methods

The phosphorus was measured using the ammonium molybdate spectrophotometric method with a ultraviolet spectrophotometer (DR4000/U, HACH company, USA). The products (PH_3) of photocatalytic reduction reaction were monitored with phosphine detector tube (7J, GASTEC, Japan). A pH meter (PHS-3C, Shanghai LeiCi instrument plant, China) was used to measure the pH of the solutions. The TEM micrograph of the photocatalyst was determined using a analytical transmission electron (TEM) (H-600 STEM/EDX PV9100, Hitachi, Japan). The specific surface area of the photocatalysts were determined by the BET nitrogen gas sorption method using a full automaticity specific surface area analyser (Gemini2360, Micromeritics, USA). The strontium content in modified TiO_2 and the compositions of the acid pickling wastewater were measured with the full spectrum of direct reading inductively coupled plasma emission spectrometer (Optima 4300DV, Perkin Elmer Ltd., USA).

All the chemicals and reagents used in this study were of analytical grade. All glassware and sample bottles were soaked in diluted HCl solution for 12 h, washed and then rinsed three times with deionized water. Deionized water was used for the preparation of solutions. All experiments were conducted in duplicate and the average values were used for data analysis. Each water quality was tested according to Water and Wastewater Monitoring and Analysis Methods (4th edition, Chinese).

3. Results and discussion

3.1. Preparation and characterization of catalysts

TEM examination of the Sr^{2+}-doped TiO_2 catalyst (Fig. 2) showed that the Sr^{2+}-doped TiO_2 catalyst had good surface properties, the average particle size of the catalyst was 8–10 nm with the presence of some smaller (5 nm) and some bigger (up to 20 nm) particles. Lv et al. [27] reported that the incorporation of Sr was in the form of strontium titanate as eutectic structure with anatase TiO_2. The specific surface area of the unmodified TiO_2 and Sr^{2+}-doped TiO_2 was found to be 65 and 78 $m^2\ g^{-1}$, respectively.

3.2. Effect of hole scavenger on photocatalytic reduction

Hole scavenger is good electron donor, the function of hole scavenger is to scavenge valence band holes. It can irreversibly combine either photo-induced hole or surface hydroxyl group, decrease the recombination degree of photogenerated electron and hole, free more reductive equivalents and enhance the effect of photocatalytic reduction [28]. So select a suitable and effective hole scavenger is essential for photocatalytic reduction. In the paper, formic acid, methanol, acetic acid, alcohol, oxalic acid and sodium oxalate were chosen as hole scavenger, Table 1 presented the effect on photocatalytic reduction of phosphorus. The reaction conditions were

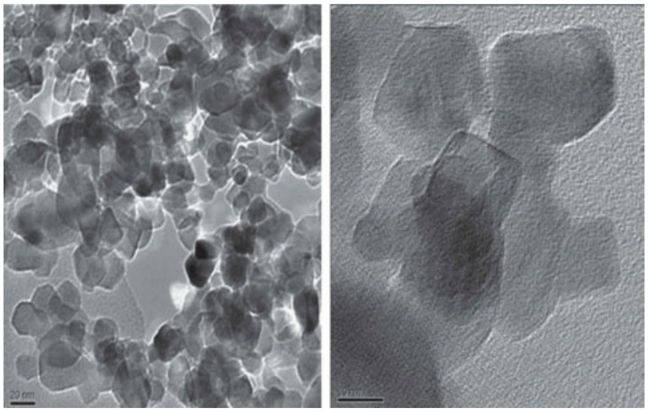

Fig. 2. TEM micrographs of the Sr^{2+}-doped TiO_2 catalysts (the length of the bar code symbol size was 20 nm).

Table 2
Influence of different hole scavengers on photocatalytic reduction of phosphorus

Hole scavenger	Without	Formic acid	Acetic acid	Methanol	Alcohol	Oxalic acid	Sodium oxalate
Removal rate (%)	58.23	99.96	99.89	99.35	99.26	99.23	99.15

as follows: the Sr^{2+}-doped TiO_2 catalyst concentration (count on TiO_2) was 2 g l^{-1}, hole scavenger concentration was 60 mmol l^{-1}, and the reaction time was 120 min.

As seen from Table 2, the phosphorus removal rate was only 58.23% without hole scavenger, and the phosphorus removal rate was increased of varying degrees under the action of the hole scavengers. The highest phosphorus removal rate was gained by using formic acid, so formic acid was selected as hole scavenger in the study.

3.3. Photocatalysis of TiO_2 for phosphorus

Several control experiments were done to evaluate the photocatalytic function of TiO_2. Table 3 described that the phosphorus removal was negligible when the experiment under high-pressure mercury lamp irradiation without TiO_2. The one without light could get the phosphorus removal rate of 49.23%, that was mainly the adsorpion effect of phosphorus on TiO_2. The experiments under high-pressure mercury lamp irradiation with or without doping Sr^{2+} proved that the photocatalytic reaction had be drastically promoted by doping TiO_2 with Sr^{2+}, that was because the crystal nucleus of Sr–TiO_2 serves as an ultramicro closed circuit photoelectrochemical cell, electrons were enriched on the metal, and the concentration of surface electrons were decreased. Accordingly, the recombination rate of photon-activated electrons and cavity was reduced and the photocatalytic activity was advanced. The gaseous product of the photocatalytic reduction was identified to be phosphine by monitoring with phosphine detector tube.

3.4. Effect of TiO_2 concentration

The effect of TiO_2 concentration on the reduction of phosphorus was drawn in Fig. 3. With increasing the concentration of TiO_2, the reduction process was accelerated (the higher removal rate of phosphorus under the same time of irradiation reached). At low TiO_2 concentrations (<2 g l^{-1}), the removal rate increased sharply with the increase of TiO_2 concentration; when the TiO_2 concentrations were higher than 2 g l^{-1}, the increase of removal rate become smooth and approached a limiting value. It could be concluded that TiO_2 concentration had powerful effect on photocatalytic reaction at low concentrations. More protons would be adsorbed on the more TiO_2 particles contained in the suspensions to accelerate the reduction process. While the transmission of light would be prevented and the reflection of light would be enhanced by the extra TiO_2 suspended in the mixture if the TiO_2 particles were much more than needed, thus the effect of the phosphorus removal was interfered. The result was consistent with the consequences of many previous documents [29,30].

Table 3
Comparison of reaction results in the presence (absence) of light and TiO_2 ([HCOOH] = 60 mmol l^{-1}, reaction time = 120 min)

Condition	TiO_2 (g l^{-1})	Sr/TiO_2	Phosphorus removal rate (%)
Light off	2	0.09%	49.23
Light on	–	–	0.12
Light on	2	–	63.35
Light on	2	0.09%	99.96

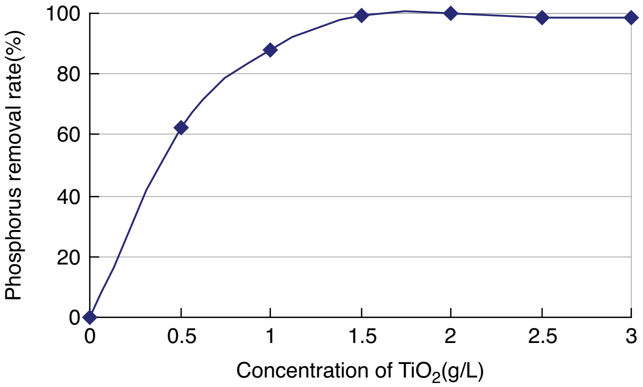

Fig. 3 The effect of TiO_2 concentration on the photocatalytic reaction. ([HCOOH] = 60 mmol l^{-1}, reaction time = 120 min).

3.5. Time course of the photocatalytic reduction

Fig. 4 showed that the phosphorus removal rate increased nearly proportionally to the irradiation time within 90 min and reached peak value at 120 min, since then the removal rate was kept basically stable. So 120 min was chosen as the optimal irradiation time in the study.

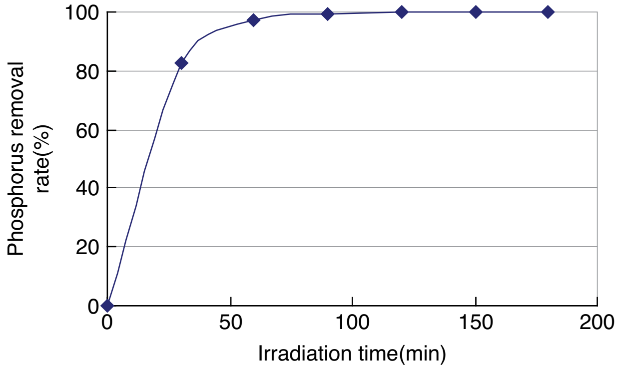

Fig. 4. Time course of the photocatalytic reduction ([TiO_2] = 2.0 g l^{-1}, [HCOOH] = 60 mmol l^{-1}).

3.6. Effect of HCOOH concentrations

The dependence of the phosphorus reduction upon the HCOOH concentration was illustrated in Fig. 5. Adsorption of some species that could trap electrons or holes played an important role in heterogeneous photocatalysis. On lowering the HCOOH concentration the phosphorus removal increased sharply with the increase of HCOOH concentration, and the maximum phosphorus removal rate was reached at the concentration of 60 mmol l^{-1}. But at high HCOOH concentration the phosphorus reduction was unsatisfactorily low. The expression may be the same mechanism of photocatalytic reduction as some inorganic ions, such as NO^{3-} [31], Se^{4+} [32] and Se^{6+} [33]. Reducing radicals COO^- and R–CH–OH were formed when HCOOH was oxidized by hydroxyl radicals or the photogenerated holes, and the former had the stronger reductive catalysts ability. The reaction rate of photocatalytic reduction would be accelerated considerably with the increase amount of formate, which was an effective photogenerated hole scavenger, when it was effectively adsorbed on the surface of TiO_2 powder. But the phosphorus adsorption on the surface of TiO_2. would be influenced by the competition of formate if the concentrations of formate were much higher than that needed, and the electrons from the conduction band was unable to be accepted by phosphorus directly. Subsequently, the reduction step would be dominated by the process of phosphorus adsorption. Therefore, the optimum HCOOH concentration was occurred for the photocatalytic reduction of phosphorus.

3.7. Effect of the initial concentrations of phosphorus and kinetic analysis

The effect of the initial phosphorus concentrations on the photocatalytic reduction was shown in Fig. 6. With decreasing the concentrations of phosphorus, the phosphorus removal was higher under the same time of irradiation. This may be attributed to the decreasing amount of phosphorus involved in the reduction that has been irradiated with more light and adsorbed on more catalysts relatively.

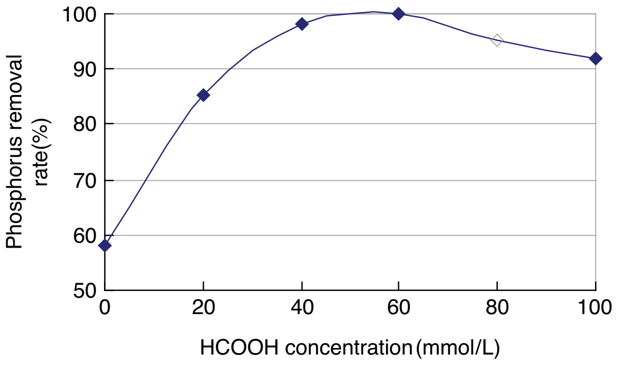

Fig. 5. The effect of HCOOH concentration on the photocatalytic reaction ($[TiO_2]$ = 2.0 g l^{-1}, reaction time = 120 min).

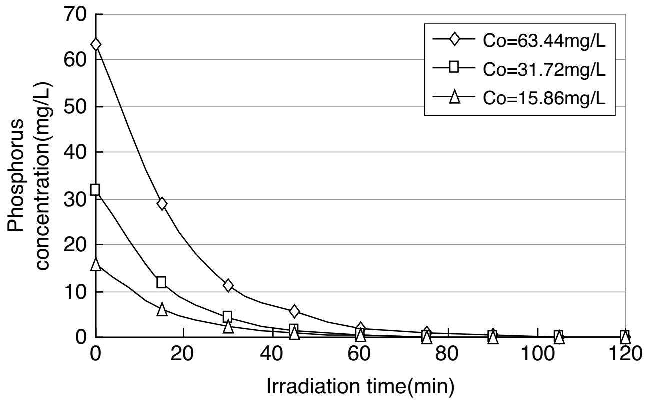

Fig. 6. Effect of the initial phosphorus concentrations on the photocatalytic reduction ($[TiO_2]$ = 2.0 g l^{-1}, [HCOOH] = 60 mmol l^{-1}).

The data in the Fig. 6 were fitted by Langmuir–Hinshelwood kinetic equation to investigate the dynamics model of photocatalytic reduction of phosphorus, and the results were shown in the Fig. 7. It was assumed that the relationship between $\ln(C_0/C)$ and irradiation time (t) was linear in the condition of different initial phosphorus concentrations, the photocatalytic reduction of phosphorus could be described by first order kinetic equation, and the reaction rate was proportional to concentration of reactants. After regression analysis, the first order kinetic equations were gained at three initial concentrations of phosphorus: when the initial concentration of phosphorus was 63.44 mg l^{-1}, $\ln(C_0/C_t) = 0.0612\ t - 0.1522$, linear relative coefficient (R^2) was

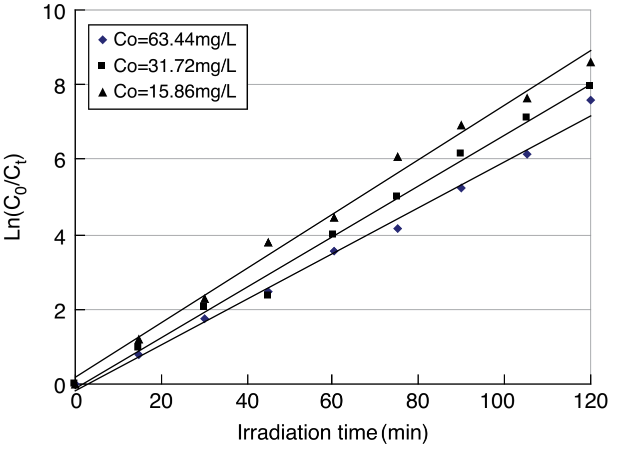

Fig. 7. Kinetic analysis of photocatalytic reduction of phosphorus.

0.9936; when the initial concentration of phosphorus was 31.72 mg l^{-1}, $\ln(C_0/C_t) = 0.0678\ t - 0.1191$, linear relative coefficient (R^2) was 0.9934; and when the initial concentration of phosphorus was 15.86 mg l^{-1}, $\ln(C_0/C_t) = 0.0727\ t + 0.2064$, linear relative coefficient (R^2) was 0.9926.

4. Conclusions

Through the experiment study, some conclusions were listed as follows:

1. The phosphorus in the acid pickling milling wastewater from high-phosphorus hematite mineral processing could be effectively treated by photocatalytic reduction with Sr-doped TiO_2 under visible light irradiation, and the gaseous product of the photocatalytic reduction was identified to be phosphine. The optimum amount of formic acid and TiO_2 were 60 mmol l^{-1} and 2.0 g l^{-1}, respectively, and the phosphorus removal could reach 99.96% when used to treat the actual mineral processing wastewater with initial pH 2.53 and phosphorus concentration 63.4 mg l^{-1}.
2. The photocatalytic reduction of phosphorus could be described by Langmuir-Hinshelwood kinetic equation, and the reaction rate was proportional to the concentration of reactants.
3. The process of photocatalytic reduction was simple and efficient with broad application prospects in the field of phosphorus-containing mine wastewater treatment, especially in the aspect of advanced treatment of phosphorus-containing wastewater.

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