Photocatalytic activity of Perovskite oxide $SrFe_{0.5}Co_{0.5}O_{3-\delta}$

for Gentian Violet

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Abstract: Perovskite-type oxide $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ was synthesized by citric acid method successfully. The structures of the catalyst were characterized by X-ray powder diffraction (XRD), scanning electron microscope (SEM).Using $SrCo_{0.5}Fe_{0.5}O_{3-\delta}$ as photocatalyst, the photocatalytic properties of degrading gentian violet (GV) were evaluated under high pressure mercury lamp. $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ exhibited higher photocatalytic activity than TiO_2, the degradation efficiency of gentian violet reached 98.09%. Several operational parameters were studied systematically, including irradiation time, photocatalyst dose, and initial gentian violet concentration. The kinetics of photocatalytic degradation of gentian violet fitted well pseudo first-order reaction with high regression coefficients R^2.

Introduction

Dye wastewater is one of the most difficult degradable industrial wastewater, due to its variety, complicated organic composition and poor biochemical degradability, even including toxic ingredients which can weaken the microbial mineralization of organic pollutants and lead to the destruction of water ecological system[1].There are various technologies investigated for the degradation of azo dyes in tradition, such as flocculation, carbon adsorption, membrane filtration, ion exchange, reverse osmosis, and advanced oxidation method[2]. Among these techniques, photocatalytic oxidation technique has been considered as a "green" and energy-saving means to degrade the soluble dyes in wastewater [3].

It is important that high activity photocatalyst was found in the photocatalytic process. Novel perovskite oxides is an p-type semiconductor photocatalyst that is highly effective to decompose organic dyes. Because these oxides utilize light energy (hv) to generate oxidation and reduction reaction[4]. Some perovskite-type oxides as photocatalysts, such as $BiFeO_3$[5], Bi_2WO_6[6] , $La_2Ti_2O_7$[7], $SrBi_2Nb_2O_9$[8], have been investigated on their photocatalytic properties and application for degrading dyes.

In this work, the perovskite oxide $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ was prepared by citric method and calcined at 850℃, and characterized by the X-ray diffractions (XRD), Scanning Electron Microscope (SEM). The photocatalytic activity of $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ was evaluated under different degrading GV conditions. The effect parameters of degradation, including irradiation time, catalyst dose were

investigated in detail. The kinetics of different concentration GV aqueous solution was determined.

Experimental

Syntheses

The perovskite oxide $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ was prepared by citric method. $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Sr(NO_3)_2$ and citrate acid were mixed and dissolved into de-ionized water, then polymerized at 90 to 100 °C for 3 to 4h. Water was evaporated by heating until the brown gel-like products were formed. The products were dried at 120 °C for 20 h and the organic compounds in the products were removed in a box furnace (Nabertherm 30-3000) at 400 °C for 2 h. The obtained black powders were ground for 0.5 h and sintered at 850 °C for 8 h. The heating or cooling efficiency was set to be 5 °C/min.

Characterizations

The structures of the powder were characterized by XRD and the figures were recorded using Dmax-RA (Rigaku) with CuKa radiation ($\lambda = 1.54$ Å) in the 2θ range of 10-80°. The sample morphology and the particle size of the fine powder were observed by SEM (TM1000, Hitachi).

Photocatalytic activity test and evaluation

The $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ powder was suspended in aqueous solution containing GV. A glass beaker filled with reacted liquid was placed vertically under a 400W high pressure mercury lamp. After a desired time intervals of irradiation, the reacted suspension was centrifuged to separate the supernatant liquid from the catalysts. The degradation efficiency under different reaction conditions, including irradiation time, catalyst dose, initial GV concentrationon the photocatalytic degradation were detected. The liquid was collected and measured by UV-vis spectrometer (Shimadzu, UV-2450).The maximum absorption $\lambda_{max} = 580$ nm.

Results and Discussion

Structure characterizations of $SrFe_{0.5}Co_{0.5}O_{3-\delta}$

The XRD patterns of the as-prepared photocatalysts $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ were shown in Fig.1. The main diffraction peak of $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ appeared in 32.78, 40.45, 47.00, 58.51, 68.71, 78.43. The main crystalline phase can be indexed on the Joint Committee on Powder Diffraction Standards (**JCPDS**) card for $SrFe_{0.5}Co_{0.5}O_3$ (JCPDS 46-0335), which was considered as perovskite oxides. The SEM image of the $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ was displayed in Fig.2. It can be seen irregular morphologies of the powders. The sample consists of the agglomeration of particles that some small size grains were adhered to the large ones. The size of the powder was estimated to be 4-18μm.

Photocatalytic degradation of GV

Effect of photocatalyst

Fig.3 showed the contrast curves of photocatalytic degradation efficiency of GV under the different degrading conditions. Compared with the curve of catalyst, it was found that the $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ exhibited excellent photocatalytic property. The degradation efficiency of GV solution was up to79.33% at irradiating 10min, while the degradation efficiency with TiO_2 was just23.2%. Seen from the curve of GV in absence of photocatalyst, the degradation efficiency of GV solution always was lower and the highest degradation efficiency only reached 6.23% for given irradiation time. $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ absorbed the light energy and generated electron/hole pairs. The OH• and $O^{\bullet-}$ radicals were originated from the reaction of photoinduced electrons (e_{CB}^-) and the reaction of photogenerated holes (h_{VB}^+) with surface absorptive OH^-, a part of the resulting holes

would react with water molecule to produce OH·[9].

Effect of photocatalyst dose

Photocatalytic degradation efficiency was measured in 10mg/L 200mL of GV aqueous solution and the photocatalyst dose was varied from 0.4g/L to 0.7g/L. As showed in Fig.4, it was observed that a photocatalytic degradation efficiency of GV almost increased with an increasing amount of photocatalyst dose, decomposed nearly completely when the 0.5g/L $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ was added into above aqueous solution for irradiation 80 min, and the photocatalytic degradation efficiency was higher than other catalyst dose. The catalyst on the surface of solution can absorbed photon and decomposed the dye molecular when the light entered dye solution [10].
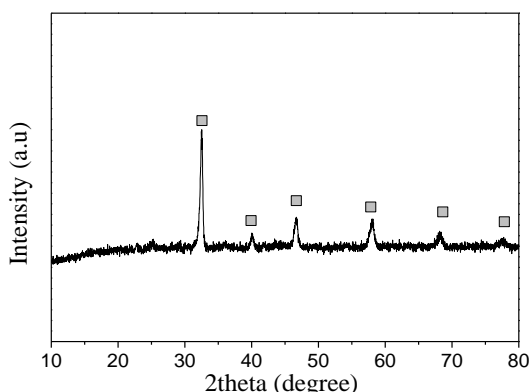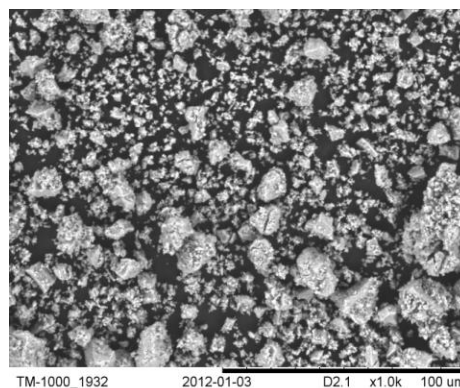

Fig.1 XRD patterns of $SrFe_{0.5}Co_{0.5}O_{3-\delta}$

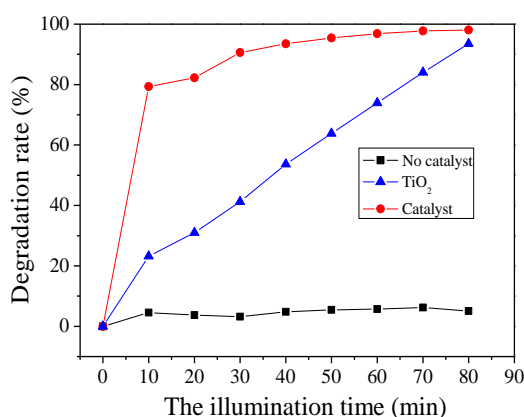
Fig.2 SEM images of $SrFe_{0.5}Co_{0.5}O_{3-\delta}$

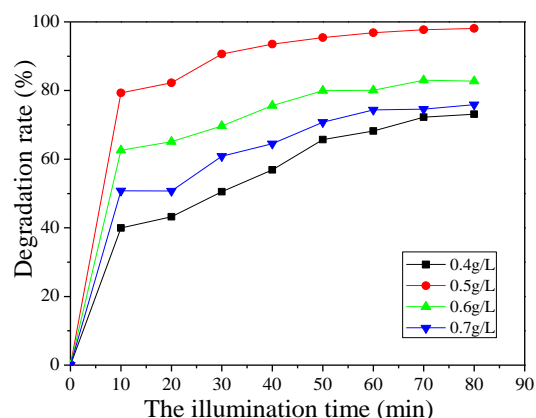Fig.3. photocatalytic degradation efficiency under different conditions

Fig.4.Effect of catalyst dose on the photocatalytic degradation efficiency of GV

Effect of initial GV concentration

The experiments were performed by varying GV initial concentrations from 6 mg/L to 14mg/L and irradiating for 80 min in 200mL 10 mg/LGV aqueous solution containing 0.6g/L catalyst. Fig.5 emerged that the photocatalytic degradation efficiency of 10mg/L GV was much higher than in other initial concentrations. As the initial concentration of dye increased, more dye molecules covered over the surface of the catalysts and therefore hindered the adsorption of the light by photocatalysts, decreasing the action of the photocatalysts. In other hand, the increase in the density of the catalyst in the area reduced the photocatalytic degradation efficiency as the initial concentration of the GV was added.

Reaction kinetics for photocatalytic reaction

In heterogeneous photocatalysis, kinetic analysis is one of the most important factors to

determine the reaction mechanism. The Langmuir-Hinshelwood model of GV degradation can be written as follows: $lnC/lnC_0=Kt+b$.

Here the rate r is proportional to the concentration, C the concentration of reactant at any time t, K is the reaction rate constant, b is the reactant adsorption constant. The regression coefficient R^2 was 0.94-0.99, which suggested the photodegradation of GV by varying the initial concentration from 6 to 14 mg/L fit well the pseudo-first-order kinetic model. The reaction rate constants of the pseudo-first-order kinetic model (kapp) was decreased from0.017 to 0.010 min^{-1}. and regression coefficients was from 0.94 to 0.99.

Conclusions

In summary, the perovskite-type structure $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ was determined by XRD analysis. The material behaved excellent photocatalytic activity and degraded effectively the GV aqueous solution. The optimum reaction conditions: 10mg/L 200 mL GV solution added 0.5g/L $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ was decomposed nearly completely for irradiation 80 min. The reaction keneics from 6mg/L to 14mg/L GV was identical with pseudo-first-order kinetics with high reaction regression coefficients.
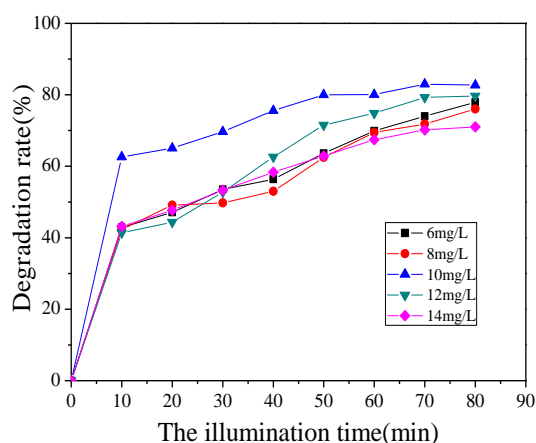

Fig.5. Effect of the catalyst concentration on the photocatalytic degradation of GV
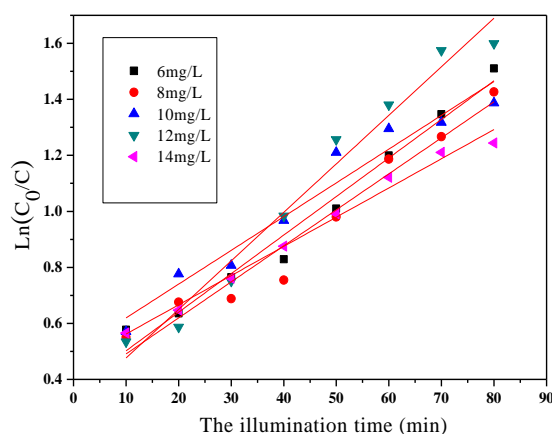
Fig.6 Kinetic curve of photocatalyst degradation for GV solution

Acknowledgements

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