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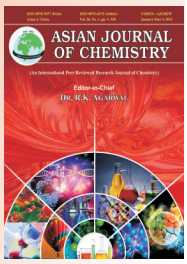

Photocatalytic Degradation of Acidic Blue Black 10B Using $SrFe_{0.5}Co_{0.5}O_{3-\delta}$

HONGYAN MENG[1,2], JUN QIAO[2] and XIANGHONG HUANG[1,2,*]

[1]School of Petrochemical Engineering, Changzhou University, Changzhou 213164, Jiangsu Province, P.R. China
[2]College of Biology and Environmental Engineering, Zhejiang Shuren University, Hangzhou 310015, Zhejiang, P.R. China

*Corresponding author: E-mail: hbeilei@126.com

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The perovskite-type oxides $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ is prepared by citrate method using strontium nitrate, iron nitrate, cobalt nitrate as raw materials. The structure of $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ is characterized by X-ray diffraction, scanning electron microscopy (SEM), Brunner-Emmet-Teller (BET) measurements. The photocatalytic properties of perovskite oxides $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ were evaluated by photocatalytic degradation of acid blue black 10B under the irradiation of UV. Several operational parameters effecting the photocatalytic degradation of acidic blue black 10B (AB) was studied systematically, including irradiation time, photocatalyst dose, acidic blue black 10B initial concentration and amount of H_2O_2 (1 %). The results showed that perovskite-type oxides $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ exhibited excellent photocatalytic properties and the degradation of acidic blue black 10B followed the pseudo-first-order kinetics.

Keywords: Photocatalytic degradation, $SrFe_{0.5}Co_{0.5}O_{3-\delta}$, Acidic blue black 10B.

INTRODUCTION

Azo dyes represent one-half of the dyes actually used in the textile industry. The reduction of azo linkages results in the production of potentially carcinogenic aromatic amines and discharge of the effluent streams from textile industries has caused serious environmental pollution[1-5]. It is urgent to develop a novel material to effectively utilizing renewable and clean solar energy to settle these puzzles[6]. Recently, great attention has been paid to develop some perovskite photocatalysts to decompose organic dyes by the technology, because the separation of electrons and holes in the perovskite oxides is easier than that in other semiconductor materials on account of their narrower depletion layers[7-9]. Moreover, it is well known that perovskite oxide samples exhibit high photocatalytic activity towards degradation of organic compounds under ultraviolet light irradiation and can work in various environments steadily[10,11] .

The preparation of perovskite photocatalysts mainly includes wet chemical methods, such as co-precipitation[12], combustion[13], sol-gel[14], sonochemical synthesis[15], thermal decomposition of the heteronuclear complex[16], microemulsion method[17] and tartaric acid method[18]. Among the various methods, citric acid method is a common and good chelating agent for metal ions to form coordination complexes. Significant advantages of this method are low temperature growth, cost effectiveness and less complicated[19].

In this study, the perovskite oxides $SrFe_{0.5}Co_{0.5}O_{3-\delta}$, which were synthesized by citric method and sintered at 850 °C, characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Brunner-Emmet-Teller (BET) measurements. Photocatalytic degradation efficiency of acidic blue black 10B (AB) in aqueous solution using $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ catalysts was evaluated under different reaction conditions, such as irradiation time, catalyst dose, initial acidic blue black 10B concentration and hydrogen peroxide amount and the optimum conditions were determinated. Additionally, the degradation studies were further confirmed by kinetic analysis.

EXPERIMENTAL

$Co(NO_3)_2.6H_2O$ (Shanghai Reagent Factory Two), $Fe(NO_3)_3.9H_2O$ (Shanghai Shisihewei chemical industry limited company), $Sr(NO_3)_2$ (Shanghai Reagent Factory Two) and 50 % excessive citric acid (Hangzhou high crystal fine chemical industry limited company) were mixed and dissolved into de-ionized water, then polymerized from 90 to 100 °C for 3 to 4 h. Water was evaporated by heating until the brown gel-like products were formed. The product was dried at 120 °C for 20 h and the organic compounds in the products were removed in a box furnace (Nabertherm P330) 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 rate was set to be 5 °C/min.

The structures of the powders were characterized by XRD and the figures were recorded using Dmax-RA (Rigaku) with CuK_α radiation ($\lambda = 1.5418$ Å) in the 2θ range of 10-80°. The sample morphology and the particle size of the fine powders were observed by SEM (TM1000, Hitachi), BET (ASAP 2020) was used to observed the specific surface area and pore size.

Photocatalytic activity: Photocatalytic degradation reaction experiments were carried out under light irradiation. The $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ powders were suspended in aqueous solution containing acidic blue black 10B. A glass beaker filled with reacted liquid was placed vertically under a 400 W 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 liquid was collected and measured by UV-visible spectrometer (Shimadzu, UV-2450). The roles of different reaction conditions, such as irradiation time, catalyst dose, initial acidic blue black 10B concentration and the amount of hydrogen peroxide solution on the photocatalytic degradation have been investigated.

The degradation efficiency was analyzed and calculated by the following equation[20]: $D(\%)=(A_0-A)/A_0 \times 100\ \%$. Where A_0 and A denote the absorbance of the dyes obtained from the UV-visible analysis at t = 0 and t = t, respectively. D represents the degradation efficiency.

RESULTS AND DISCUSSION

Structural characterization 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 showed in Fig. 1. Six distinctive peaks occurred at 32.78°, 40.45°, 47.00°, 58.51°, 68.71° and 78.43°. The main crystalline phase can be indexed on the basis of a perovskite $SrFe_{0.5}Co_{0.5}O_3$, cubic structure by comparison with the data from the Joint Committee on Powder Diffraction Standards (JCPDS) card for $SrFe_{0.5}Co_{0.5}O_3$ (JCPDS 46-0335).

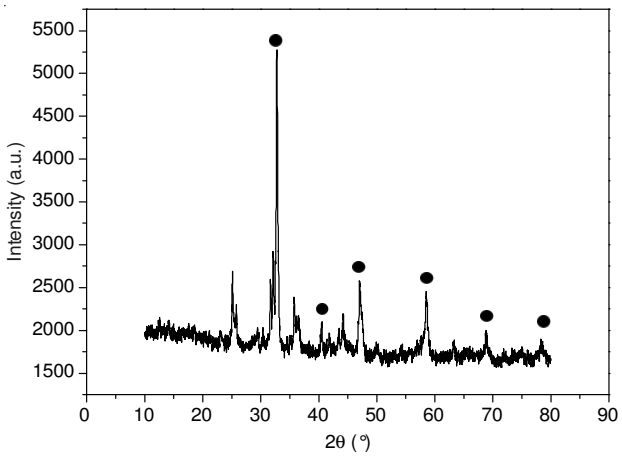

Fig. 1. XRD patterns of the prepared sample

The SEM images of the $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ with different magnifications were 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. This was ascribed to sintering a big chuck of cross-linked polymer formed by citrate process. The size of the powder was estimated to be 5-18 μm.

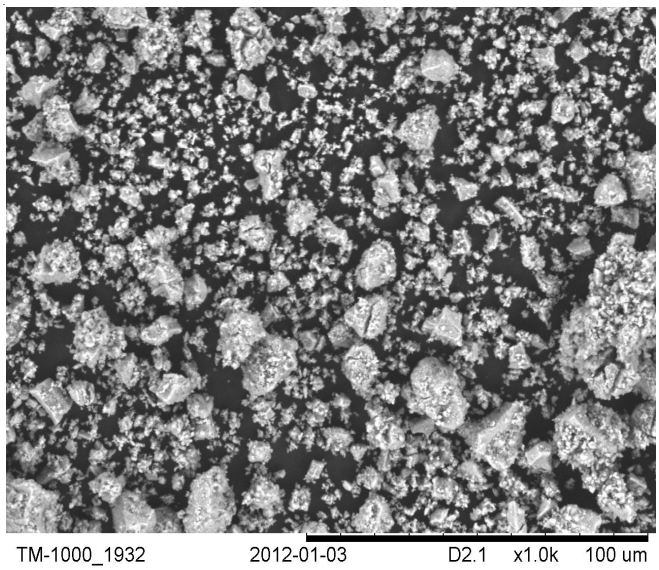

Fig. 2. SEM images of the prepared sample

The average pore size of $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ was 26.42 nm and the specific surface area was 22.25 m^2/g measured by N_2 absorption-desorption isotherms.

Photocatalytic degradation activity of acidic blue black 10B

Effect of the irradiation time: The effect of the irradiation time was investigated from 10 to 65 min in 200 mL 10 mg/L acidic blue black 10B solution using 0.1 g $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ (Fig. 3). The degradation efficiency increased sharply from 10 to 50 min and then increased slowly with extending irradiation time. The photocatalytic activity of $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ was better than that without catalyst experiment under the same reaction condition. It can be explained that more acidic blue black 10B molecules were degraded with extending the irradiation time because light energy was absorbed in the acidic blue black 10B solution. The highest value reached 98.58 % using $SrFe_{0.5}Co_{0.5}O_{3-\delta}$.

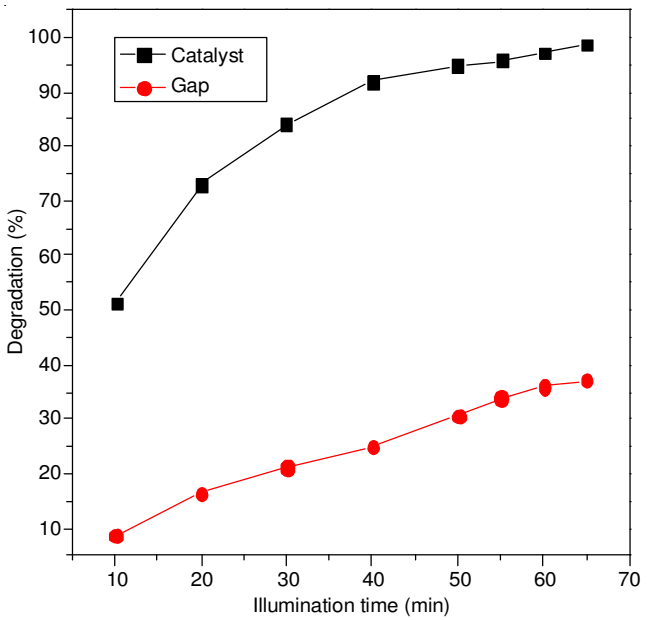

Fig. 3. Effect of the irradiation time on the photocatalytic degradation efficiency of acidic blue black 10B

Effect of the photocatalyst dose: Fig. 4 exhibited the photocatalytic degradation efficiency of acidic blue black 10B using different catalyst doses. It can be seen that degradation efficiency increased with extending irradiation time in general. The maximum efficiency of degradation acidic blue black 10B is 89.2, 95.37, 96.09 and 97.66 % when 0.06, 0.08, 0.10, and 0.12 g $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ is respectively added to the 200 mL acidic blue black 10B aqueous solution. However, the maximum degradation efficiency is only 85.25 % using 0.14 g $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ in the same way. The photocatalytic degradation efficiency can increased with increasing the catalyst dose at a certain range. However, it's not obvious when continued to increase dose of catalyst after 0.12 g. The reaction may be that the improvement of the degradation efficiency was attributed to the increase of the availability of the active sites in the density of particles, increasing the number of the adsorbed dye molecules[21]. A number of catalysts resulted in the agglomeration of the activated molecules and decreased the radiation penetration.

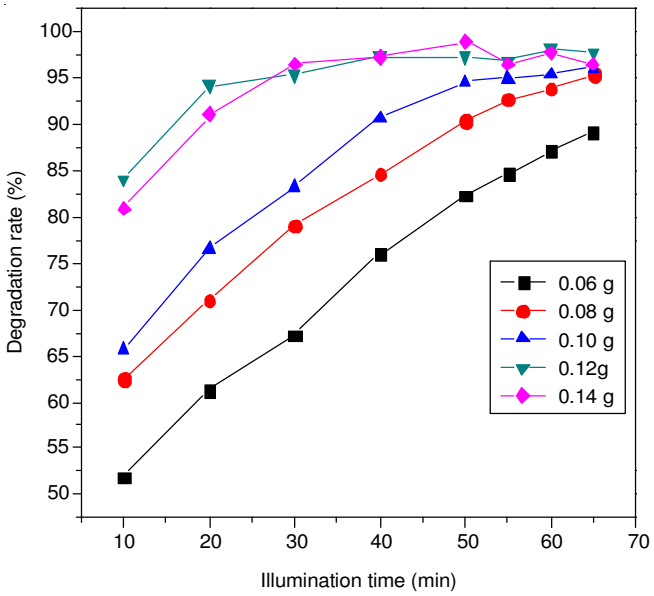

Fig. 4. Effect of catalyst dose on the photocatalytic degradation efficiency of acidic blue black 10B

Effect of initial acidic blue black 10B concentration: The experiments were performed by varying dye initial concentrations from 5 to 15 mg/L and irradiating for 65 min in 200 mL 10 mg/L acidic blue black 10B aqueous solution containing 0.12 g catalyst. Fig. 5 exhibited the photocatalytic degradation efficiency of the acidic blue black 10B in various initial concentrations. From the curves it could be found that degradation efficiency increased with extending irradiation time The maximum degradation efficiency was 94.49, 93.78, 91.64, 81.04 and 77.03 %, respectively when the initial concentration of acidic blue black 10B was 5, 7.5, 10, 12.5, 15 mg/L. The greater concentration increased, the lower photocatalytic efficiency became. 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

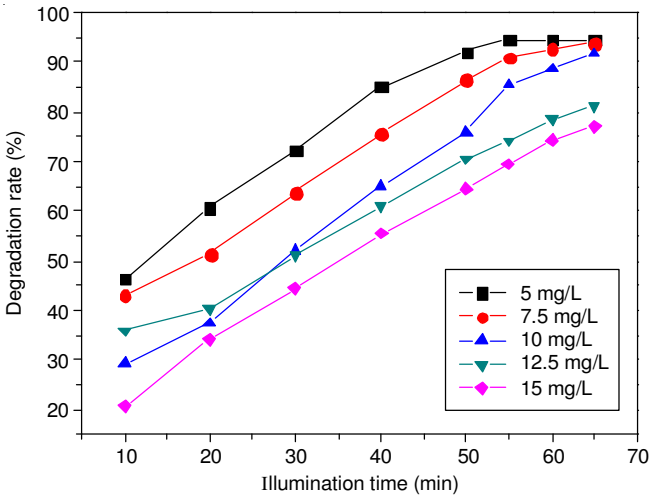

Fig. 5. Effect of the initial catalyst concentration on photocatalytic degradation efficiency of acidic blue black 10B

reduced the photocatalytic degradation efficiency as the initial concentration of the acidic blue black 10B was higher[22].

Effect of the amount of hydrogen peroxide solution: The experiments were performed by varying the amount of H_2O_2 (1 %) from 0.1 to 0.5 mL irradiating for 65 min in 200 mL 10 mg/L acidic blue black 10B aqueous solution containing 0.12 g catalyst. The effect of H_2O_2 on the photocatalytic degradation of the acidic blue black 10B was displayed in Fig. 6. From the curves it could be found that the dissolved oxygen in acidic blue black 10B solution was saturated generally and the highest degradation efficiency was 99.15 % until containing 0.2 mL irradiating for 65 min was a strong oxidant that can generate some strong oxidative free radical $^{\bullet}OH$. Meanwhile, as electron capture agents, H_2O_2 can reduce the composite photo-generated electrons and holes and promote photocatalytic degradation.

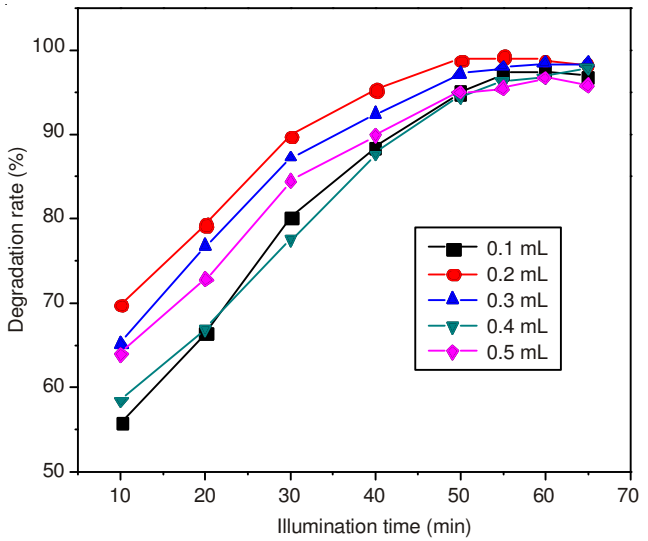

Fig. 6. Effect of the H_2O_2 amount on the the photocatalytic degradation efficiency of acidic blue black 10B

Reaction kinetics for catalysts: In heterogeneous photocatalysis, kinetic analysis is one of the most important factors to determine the reaction mechanism. Photocatalytic degradation of acidic blue black 10B follows pseudo-first-order

kinetics in agreement with the Langmuir-Hinshelwood mechanism. The Langmuir-Hinshelwood model of acidic blue black 10B degradation can be written as follows:

$$r = kKC_t / 1 + KCt \approx k_{app}C_t$$

here the rate r is proportional to the concentration, C_t is the concentration of reactant at any time *t*, k_{app} is the reaction rate constant, K is the reactant adsorption constant. The straight line confirms that the degradation of acidic blue black 10B follows the pseudo-first-order kinetics (Fig. 7). The regression coefficient R^2 was 0.970-0.990, which suggested the photodegradation of acidic blue black 10B by varying the initial acidic blue black 10B concentration from 5 to 15 mg/L fit the Langmuir-Hinshelwood kinetic model. The reaction rate constants and regression coefficients of photocatalytic degradation were calculated and the results were shown in Table-1. As can be seen from Table-1, the reaction rate constants of the pseudo-first-order kinetic model (k_{app}) was decreased from 0.047 to 0.023 min^{-1} with increasing initial acidic blue black 10B concentration from 5 to 15 mg/L[23-25].

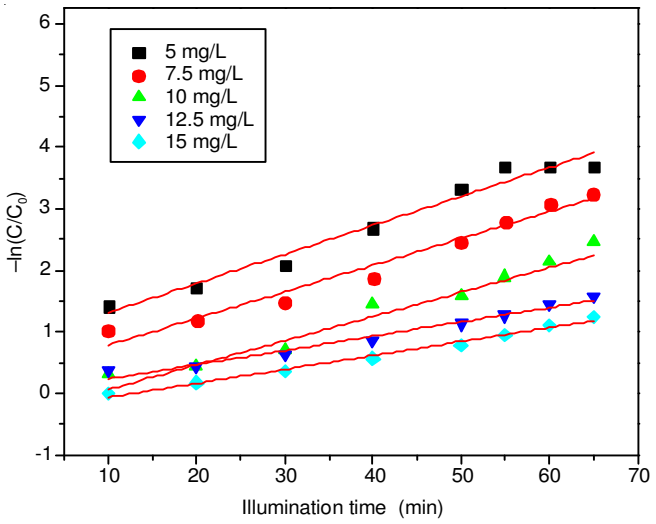

Fig. 7. Reaction kinetics for the photocatalytic degradation of the acid blue-black

TABLE-1

Concentration (mg/L)	Rate constant K_{app} (min^{-1})	R^2
5	0.047	0.972
7.5	0.043	0.970
10	0.040	0.970
12.5	0.023	0.976
15	0.023	0.990

Conclusion

The peroskite-type oxides $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ can degrade effectively acidic blue black 10B solution under light irradiation and exhibited higher photocatalytic activity. The highest photocatalytic degradation efficiency was 94.49 % when the initial acidic blue black 10B concentration was 5 mg/L acidic blue black 10B solution containing 0.12 g $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ irradiating for 65 min. The optimum irradiation time, photocatalyst dose, acidic blue black 10B initial concentration and the amount of H_2O_2 were 65 min, 0.12 g, 5 mg/L and 0.2 mL in 200 mL acidic blue black 10B aqueous solution with $SrFe_{0.5}Co_{0.5}O_{3-\delta}$, respectively. The photocatalytic degradation reaction kinetics of acidic blue black 10B by varying the initial acidic blue black 10B concentration from 5 to 15 mg/L fit the Langmuir-Hinshelwood kinetic model.

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