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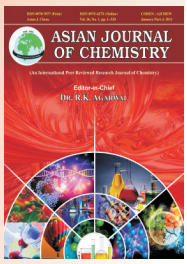

# Photocatalytic Degradation of Gentian Violet Using $Ba_xSr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$

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Perovskite oxides $Ba_xSr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$ (x = 0.2, 0.4) were synthesized by citrate method. The structures and the morphology of the prepared samples were characterized by X-ray diffraction and scanning electron microscopy. The photocatalytic degradation property of Gentian violet in aqueous solution was investigated using $Ba_xSr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$ as the photocatalysts. The effects of irradiation time, catalyst dose, initial concentration and pH value on the degradation were explored systematically under the irradiation of a 400 W high pressure mercury lamp. The optimum reacted conditions were that irradiation time was 60 and 80 min, catalyst dose 0.2 and 0.22 g in 100 mL10 mg/L Gentian violet solution using $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$ and $Ba_{0.4}Sr_{0.6}Fe_{0.5}Co_{0.5}O_{3-\delta}$, respectively, initial concentration and pH value were Gentian violet 5 mg/L and 3.08 for both photocatalysts.

**Keywords: $Ba_xSr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$, Gentian violet, Photocatalytic degradation, Influence factors.**

## INTRODUCTION

Heterogeneous photocatalysis represents a healthy and clean technique for environmental application in wastewater treatment[1-5]. Firstly, oxidation-reduction process occurs simultaneously in this process. The process can destroy the polluting compounds by decomposing into non-toxic substances with light irradiation. Secondly, the whole photocatalytic process can be performed under mild conditions, such as room temperature and atmospheric pressure. Thirdly, some environmental friendly materials are applied as photocatalysts. Fourthly, the process brings about the complete degradation of most organic pollutants without secondary pollution. Fifthly, photocatalysts with rare earth oxides are non-toxic and have good chemical stability. Finally, to date, great attention has been devoted to the photocatalysis because of the use of sunlight as the clean and renewable source of irradiation.

Titanium dioxide ($TiO_2$) has been used widely in photocatalysis due to its chemical stability and low cost in the ultraviolet light region[6-7], many efforts have been devoted to its optical response [8-11]. In order to develop new photocatalysts induced at broaden the wavelength, several researchers have paid great attention to perovskite metal oxides, such as $BiFeO_3$, $NaTaO_3$, $NiMoO_4$, $Bi_2Ti_4O_{11}$, $Bi_2WO_6$, $Bi_2W_2O_9$, $KNb_3O_8$, $K_4Nb_6O_{17}$, $La_2Ti_2O_7$ and $Bi_2MoO_6$[12-21].

Perovskite metal oxides can increase the quantum efficiency of heterogeneous photocatalytic properties by action of electron/hole and enhance the photocatalytic activity. In this study, $Ba_xSr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$ (x = 0.2, 0.4) synthesized by citrate method and sintered at 850 °C were characterized by X-ray diffraction and scanning electron microscopy. Photocatalytic degradation of Gentian violet in aqueous solution using $Ba_xSr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$ was performed by light irradiation. The influence factors, such as irradiation time, catalyst dose, initial concentration and pH value of Gentian violet solution on the photocatalytic activity, were also explored systematically.

## EXPERIMENTAL

$Sr(NO_3)_2$, $Co(NO_3)_2{\cdot}6H_2O$ (A.R. grade, Shanghai Reagent Factory Two Co. Ltd.); $Ba(NO_3)_2$ (A.R. grade, Chemical Experiment Factory of Shanghai College ); $Fe(NO_3)_3{\cdot}9H_2O$ (A.R. grade, Shanghai Shenbo Chemical Co. Ltd.); Citric acid $C_6H_8O_7{\cdot}H_2O$ (A.R. grade, Hangzhou Gaojing Fine Chemical Co.Ltd.); Gentian violet $C_{25}H_{30}ClN_3$ (A.R. grade, Shanghai Specimen Model Factory Co. Ltd.).

**General procedure:** Four stoichiometric nitrates (Ba, Sr, Fe, Co nitrates) and 50 % excessive citric acid were mixed and dissolved into de-ionized water and were polymerized at 90-100 °C for 3-4 h. Then water was evaporated by heating until brown gel-like products were formed. The gel-like products were placed in a box furnace (Nabertherm 30-3000) at 120 °C for 20 h and then were maintained at 400 °C for 2 h to remove the organic compounds. The heating or cooling rate was 5 °C/min. The obtained powders were ground for 0.5 h and sintered at 850 °C for 8 h.

**Detection method:** The structures of the powders were characterized and analyzed by XRD recorded by Dmax-RAv (Rigaku) using $CuK_\alpha$ radiation ($\lambda = 0.15418$ nm). The samples were scanned in the 2θ range of 10-90°. SEM (TM1000, Hitachi) was used to observe the morphology and size of the powders.

## RESULTS AND DISCUSSION

Fig. 1 showed the XRD patterns of the $Ba_xSr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$ (x = 0.2, 0.4) powders in the 2θ range of 10-90°. Perovskite-type structure could be found from the two samples. However, no pure cubic structure could be observed because of the doping of Ba. The result was consistent with those reported by Shao *et al.*[22]. Compared with the two patterns of the samples, the XRD patterns of $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$ behave smaller tilt peaks and display purer cubic structure.

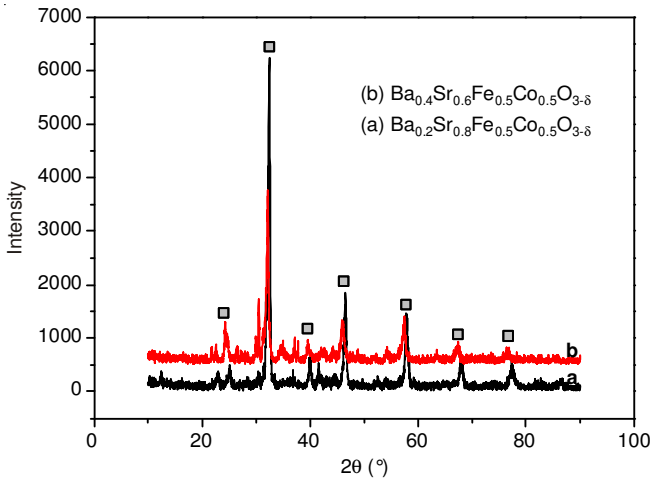


Fig. 1. XRD patterns of the prepared samples, (a) $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$, (b) $Ba_{0.4}Sr_{0.6}Fe_{0.5}Co_{0.5}O_{3-\delta}$

Fig. 2 showed the SEM images of the $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$ and $Ba_{0.4}Sr_{0.6}Fe_{0.5}Co_{0.5}O_{3-\delta}$. Irregular morphologies of the powders were observed from the SEM images. The two samples consist of the agglomeration of particles that some small size grains were adhesive to the large ones. This was ascribed to sintering a big chuck of cross-linked polymer formed by citrate process[23]. The size of the two powders was estimated to be 1-10 μm.

**Photocatalytic degradation of photocatalyst:** The solution of 10 mg/L Gentian violet was scanned under λ from 400 to 600 nm with UV-visible spectrometer. Fig. 3 showed the absorption curve of the Gentian violet. It was found that the maximum adsorption wavelength was 581 nm and the maximum absorbance was 0.72 which was acted as $A_0$.

**Effect of the irradiation time on the photocatalytic degradation:** Experiments were performed in 100 mL 10 mg/L Gentian violet solution using 0.2 g $Ba_xSr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$ at different irradiation time. The effect of the irradiation time on the photocatalytic degradation was shown in Fig. 4. It was observed that the photocatalytic degradation efficiency of the Gentian violet increased sharply with the increasing irradiation time from 10 to 60 min using $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$ and from 10 to 80 min using $Ba_{0.4}Sr_{0.6}Fe_{0.5}Co_{0.5}O_{3-\delta}$, respectively. From these results, the highest value reached 98.05 % using

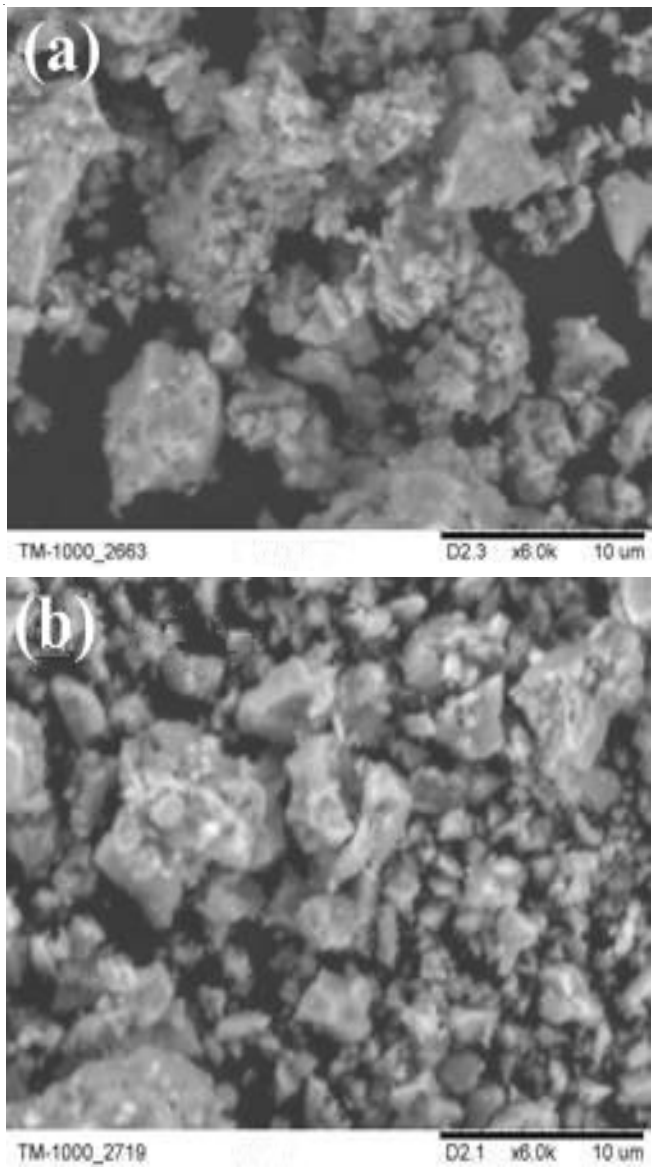


Fig. 2. SEM images of the samples, (a) $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$, (b) $Ba_{0.4}Sr_{0.6}Fe_{0.5}Co_{0.5}O_{3-\delta}$

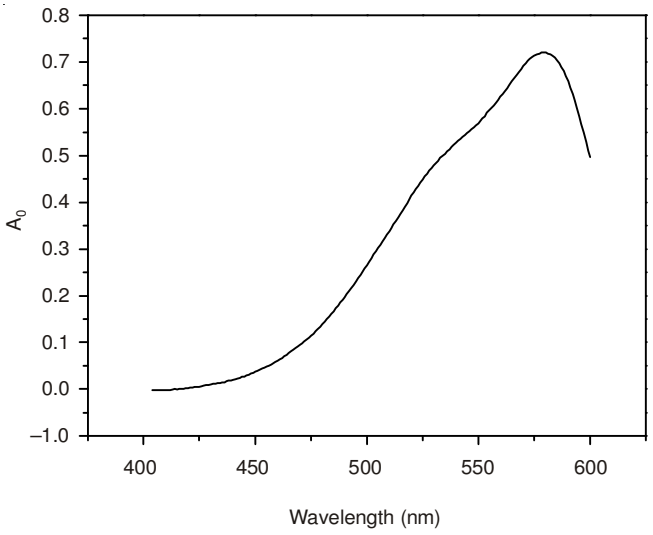


Fig. 3. UV-visible spectrum of the Gentian violet

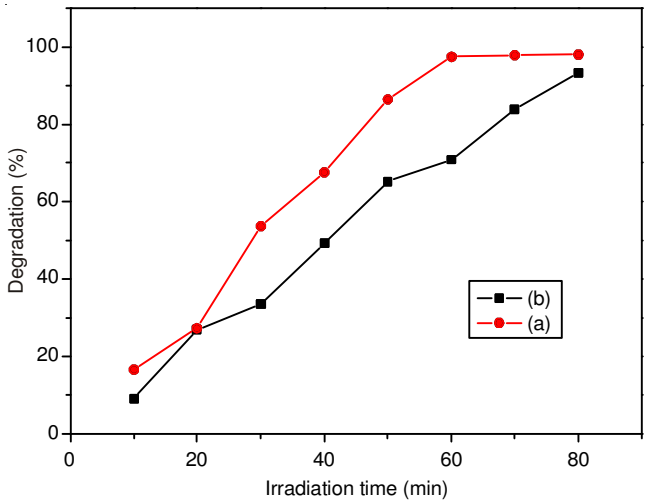


Fig. 4. Effect of the irradiation time on the photocatalytic degradation of Gentian violet, (a) $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$, (b) $Ba_{0.4}Sr_{0.6}Fe_{0.5}Co_{0.5}O_{3-\delta}$

$Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$ and 93.19 % using $Ba_{0.4}Sr_{0.6}Fe_{0.5}Co_{0.5}O_{3-\delta}$ after irradiating for 80 min, respectively. It can be explained that more Gentian violet molecules were degraded with extending the irradiation time because light energy was absorbed in the Gentian violet solution. Compared with the two curves, $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$ behaved better photocatalytic degradation property after irradiating for 20 min than that of $Ba_{0.4}Sr_{0.6}Fe_{0.5}Co_{0.5}O_{3-\delta}$.

**Effect of the photocatalyst dose on photocatalytic degradation:** In order to analyze the optimum dose of the photocatalysts, the experiments were carried out in 100 mL 10 mg/L Gentian violet solution using perovskite-type $Ba_xSr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$ irradiating for 1 h. From (Fig. 5), it was found that the photocatalytic degradation efficiency of the Gentian violet increased with the increasing amount of the photocatalysts. The photocatalytic degradation efficiency of the Gentian violet reached the highest degradation efficiency of 97.50 % and 95.42 % when the amount of $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$ and $Ba_{0.4}Sr_{0.6}Fe_{0.5}Co_{0.5}O_{3-\delta}$ was 0.20 g and 0.22 g, respectively. However, the degradation efficiency seemed to gradually come close to limit after loading more catalysts. This phenomenon is similar to the degradation behavior using other photocatalysts[18,24].

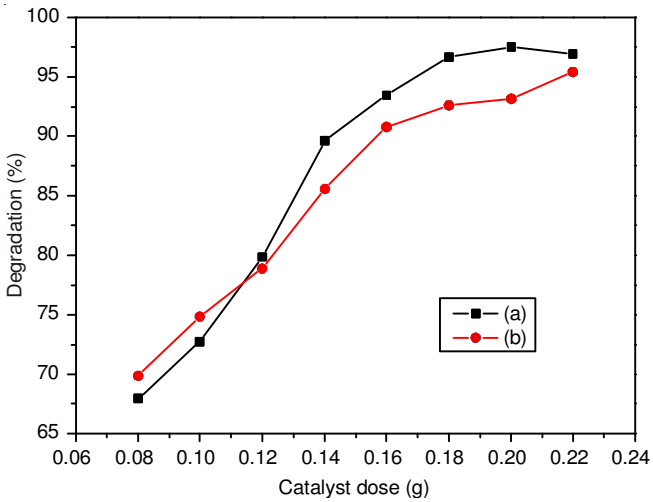


Fig. 5. Effect of the catalyst dose on the photocatalytic degradation of Gentian violet, (a) $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$, (b) $Ba_{0.4}Sr_{0.6}Fe_{0.5}Co_{0.5}O_{3-\delta}$

The enhancement 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[25]. Higher catalysts resulted in the agglomeration of the activated molecules and decreased the radiation penetration.

**Effect of the initial Gentian violet concentration on photocatalytic degradation:** The experiments were performed by varying dye initial concentrations from 5 to 20 mg/L and irradiating for 50 min in 100 mL of 10 mg/L Gentian violet aqueous solution containing 0.20 g catalyst. Fig. 6 exhibited the photocatalytic degradation efficiency of the Gentian violet in various initial concentrations. From the curves it could be found that the photocatalytic degradation was better at lower initial concentration of Gentian violet and reached the highest value when the initial concentration was 5 mg/L. The degradation efficiency decreased rapidly when the initial concentration of the dyes was higher than 10 mg/L. 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 Gentian violet was increased [26]. Comparison with the two curves, $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$ displayed higher photocatalytic activity of the Gentian violet.

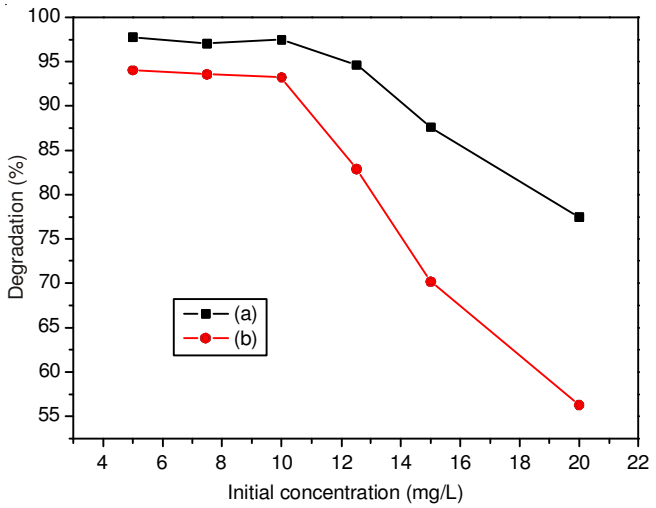


Fig. 6. Effect of the initial concentrations on the photocatalytic degradation of Gentian violet, (a) $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$, (b) $Ba_{0.4}Sr_{0.6}Fe_{0.5}Co_{0.5}O_{3-\delta}$

**Effect of the pH on the photocatalytic degradation:** The effect of the pH from 3.08 to 10.91 on the photocatalytic degradation in 100 mL of 10 mg/L Gentian violet aqueous solution containing 0.20 g $Ba_xSr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$ irradiating for 1 h was illustrated in Fig. 7. The photocatalytic degradation efficiency dropped quickly with increasing the pH value. $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$ displayed higher photocatalytic activity than $Ba_{0.4}Sr_{0.6}Fe_{0.5}Co_{0.5}O_{3-\delta}$ when the pH value was in the range of 3.08-6.95 and 8.8-10.91, respectively. However, $Ba_{0.4}Sr_{0.6}Fe_{0.5}Co_{0.5}O_{3-\delta}$ exhibited slightly better degradation ability when the pH range was from 6.95 to 8.8. The highest degradation efficiency was 97.50 % using $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$

and 93.19 % using $Ba_{0.4}Sr_{0.6}Fe_{0.5}Co_{0.5}O_{3-\delta}$ when the pH was 3.08, respectively.

The electron and hole pairs formed from the interlayer space of the perovskite-type compounds by photo-absorption. The relevant reactions resulting in the degradation of the Gentian violet can be expressed as follows[27].

$$\text{Photocatalyst} + h\nu \longrightarrow e^- + h^+ \quad (1)$$

$$h^+ + H_2O \longrightarrow {}^\bullet OH + H^+ \quad (2)$$

$$h^+ + OH^- \longrightarrow {}^\bullet OH \quad (3)$$

The alkaline group of the Gentian violet might combine with positive ions at low pH and produce more active group ($^\bullet$OH) which played an important role in the photocatalytic degradation dye process. Hence, the recombination of the excited electrons and positive holes could be retarded in Gentian violet solution with low pH value and be beneficial to photocatalytic degradation.

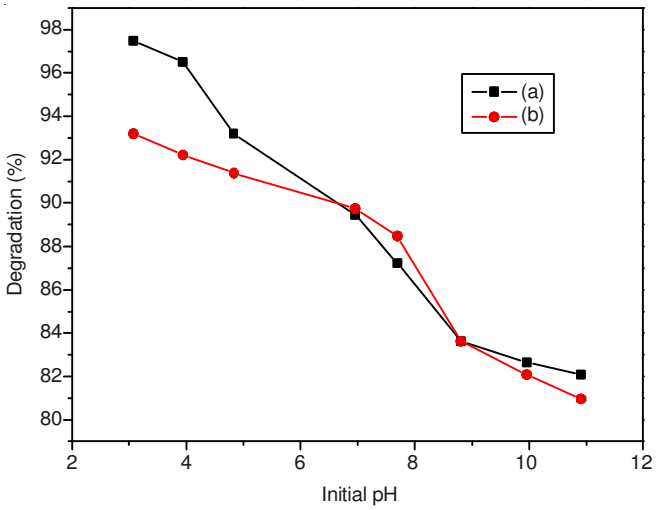


Fig. 7. Effect of the pH value on the photocatalytic degradation of the Gentian violet, (a) $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$, (b) $Ba_{0.4}Sr_{0.6}Fe_{0.5}Co_{0.5}O_{3-\delta}$

## Conclusion

The peroskite-type oxides $Ba_xSr_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$ can degrade effectively the Gentian violet under light irradiation. Various reaction parameters, *i.e.*, irradiation time, catalyst dose, initial concentration of the Gentian violet and initial pH value of solution were systematically studied in the experiments of the photocatalytic degradation in the Gentian violet aqueous solution. The highest photocatalytic degradation efficiency was 98.05 % when the initial Gentian violet concentration was 10 mg/L containing 0.2 g $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$ irradiating for 1 h under 400 W high pressure mercury lamp. However, the best degradation efficiency was 95.41 % in 100 mL of 10 mg/L Gentian violet solution containing 0.2 g $Ba_{0.4}Fe_{0.6}Sr_{0.5}Co_{0.5}O_{3-\delta}$ irradiating for 80 min. And the optimum pH value was 3.08 in 100 mL of 10 mg/L Gentian violet aqueous solution. $Ba_{0.2}Sr_{0.8}Fe_{0.5}Co_{0.5}O_{3-\delta}$ and $Ba_{0.4}Fe_{0.6}Sr_{0.5}Co_{0.5}O_{3-\delta}$ exhibited higher photocatalytic activity of degrading Gentian violet.

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