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Original Research

Homogeneous Photocatalytic Iron Slag Reduction Cr^{6+} from Chromium Wastewater Containing High-Salt in Constructed Wetland

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Abstract

The reductive removal of hexavalent chromium Cr^{6+} by iron slag from aqueous solutions was investigated. Iron slag was treated with a grinding miller and washed thoroughly. The redox reaction of iron slag onto the chromium Cr^{6+} was initiated by Fenton's reagent (Fe^{2+}/H_2O_2). The optimum conditions for adsorption of Cr^{6+} were found to be as follows: pH 3; photocatalyst dose 0.13 g/L; COD 400 mg/L; Cl^- concentration 5 mg/L; matrix was gravel and construction waste and contact; reaction time was 270 min. In addition, the action mechanism of each factor in the wastewater was analyzed. In the reaction system, pH was the main influencing factor. When the pH was 3, the reduced rate of Cr^{6+} could reach 99%. High salinity had a certain effect on Cr^{6+} reduction. When the Cl^- concentration was more than 6 mg/L, Cr^{6+} reduction rate was below 90%. Owing to high efficiency and low cost, iron slag could be used as an effective catalyst for Cr^{6+} removal from wastewater.

Keywords: constructed wetlands, photocatalytic, chromium Cr^{6+}, high-salt-containing chromium wastewater

Introduction

Industrial effluents containing heavy metals are major contributors to water pollution [1, 2]. The use of chromium is quite widespread and it is used in wood preservation, textile dyeing, pigments, pulp, metal plating, petroleum refining, the steel industry, tanning, finishing of metals and plastics [1-4], etc. As a result, its concentration in the environment, particularly in water bodies, has increased from its natural abundance during the last two decades [5].

Chromium exists in aqueous media as two oxidation states: hexavalent Cr^{6+} and trivalent Cr^{3+}. The toxicity of chromium depends on its oxidation state. When low levels are present in the environment, trivalent chromium apparently plays an essential role in plant and animal metabolism [6], while hexavalent chromium is directly toxic to bacteria, plants and animals suspected to be carcinogenic [7-13]. Bugajski et al. [14] reported that with respect to the average daily flow of wastewater at the level of 13700 $m^3 \cdot d^{-1}$, it was found that in 1 m^3 of wastewater there is almost 0.01 kg of chromium compounds. Trivalent and hexavalent forms in aqueous systems cause diarrhea, and according to WHO (the World Health Organization), its permissible level in surface water bodies is 0.05 mg/L and its

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concentration in industrial wastewater varies from 0.5 to 270 mg/L. Thus it is mandatory to treat Cr-bearing wastewater.

High-salt wastewater is produced by several industrial processes. including food processing, wine production, tanning, textile production, aquaculture, and oil production [15]. Treatment of these wastewaters is necessary to reduce pollution and prevent eutrophication; high-salt wastewater is one of the major problems in the wastewater treatment industry. Previous studies showed that the high salinity can have an effect on microorganism uptake and releasing phosphorus by biological cells, and on the dissolution from biomass into the liquid phase. Most microorganisms are unable to cope with a high salinity environment; they will die or become dehydrated and dormant [16], consequently causing difficulties in biodegradation for the saline wastewater [17-18]. In addition, salinization poses one of the greatest threats to our rivers and wetlands, and it has the potential to cause irreversible damage to the structure and function of aquatic communities in arid regions of the world [19].

Photocatalytic degradation of pollutants is a kind of advanced oxidation process (AOP). The concept of advanced oxidation technology was first proposed by Glaze et al. [20]. In the process of water treatment, various modern technologies are applied to mineralize toxic and harmful organics that are difficult to solve by technologies such as biogasification to non-toxic and harmless levels. At present, the main methods to deal with contaminants include chemical precipitation, ion exchange, ultra-filtration, reverse osmosis, and adsorption. However, these methods have some limitations due to the production of secondary wastes, a large quantity of slug formation and high operational costs [21-24]. Conversely, the photocatalytic method is more advantageous than the other methods due to its simple operation design with a sludge-free environment and low cost. Compared to the traditional environmental pollution material treatment methods, the advantages of photocatalytic technology are reflected in the following aspects: (1) as the advanced oxidation technology, photocatalytic technology can completely mineralize and decompose organic materials without causing secondary pollution; (2) photocatalytic utilization is clean, renewable solar energy, low cost and great potential for development; (3) the photocatalytic reaction is comfortable, it can be carried out at natural temperatures, and the device is relatively simple and the application scope is wide; (4) the common photocatalyst is usually non-toxic and low price. Therefore, we think that photocatalysis will inevitably be a tremendous contribution to energy and environmental issues in the development of human civilization.

Constructed wetlands are engineered wetlands that have been designed and constructed to mimic natural wetland systems for treating wastewater. The system mainly comprises wetland vegetation, substrates, soils, water and their associated microbial assemblages, which utilize complex processes involving physical, chemical, and biological mechanisms to remove various contaminants or improve water quality [25-26]. A constructed wetland wastewater treatment system has the advantages of stable water quality, low investment, low energy consumption, simple operation and low operating costs.

The photocatalysis-constructed wetland combination wastewater treatment technology has the advantage of stable water quality, lower investment, and low operating cost. At the same time, this combination of technology and environmental ecology technologies have effectively treated wastewater and provided an ecological landscape, which brought a certain economic benefit. This experiment mainly discusses the reaction mechanism of photocatalytic reduction Cr^{6+} and the effect of the iron slag as the catalyst, light conditions, pH, Cl^-, COD and the substrates on the reduction of Cr^{6+} in the constructed wetland wastewater.

The constructed wetland system is composed of water, hydrophyte plants, substance, etc. This study is the basic research of the photocatalysis-constructed wetland system. Analyzing the physiological and biochemical characteristics of plants and optimizing the photocatalytic and ecological combination method for the treatment of chromium wastewater containing high-salt is the develop research of the photocatalytic constructed wetland system.

The purpose of the study was to determine the best conditions for chromium wastewater treatment of the homogeneous photocatalytic in constructed wetlands without hydrophyte plants.

Materials and Methods

Experimental Design

The experiments were conducted in a greenhouse of the Shanghai Institute of Technology (Shanghai, China). The simulated wastewater was configured according to the tannery's secondary effluent water quality. All the use chemicals in this study were reagent grade. $K_2Cr_2O_7$ was utilized as the source of Cr^{6+}, and all beakers and bottles used in the experiments were washed with 5% HCl and covered with aluminum foil to prevent photooxidation or photoreduction. In this study, Cr^{6+} concentration in the water samples was 1.5 mg/l and the Cl^- concentration was 5 mg/l. The catalyst is iron slag, of which the iron content is 80%. H_2SO_4 and NaOH were used in the experiment to adjust the pH of the reaction system.

The reaction vessel is a 30 cm high plastic bucket whose diameter is 20 cm, which is covered by a black shading. The UV light part is designed as a GGZ-175W high-pressure mercury lamp UV lamp with an external insulation quartz sealed glass sleeve inserted into the water body (Fig. 1), and fixed on the cover, a design that is conducive to the use of light sources. There is

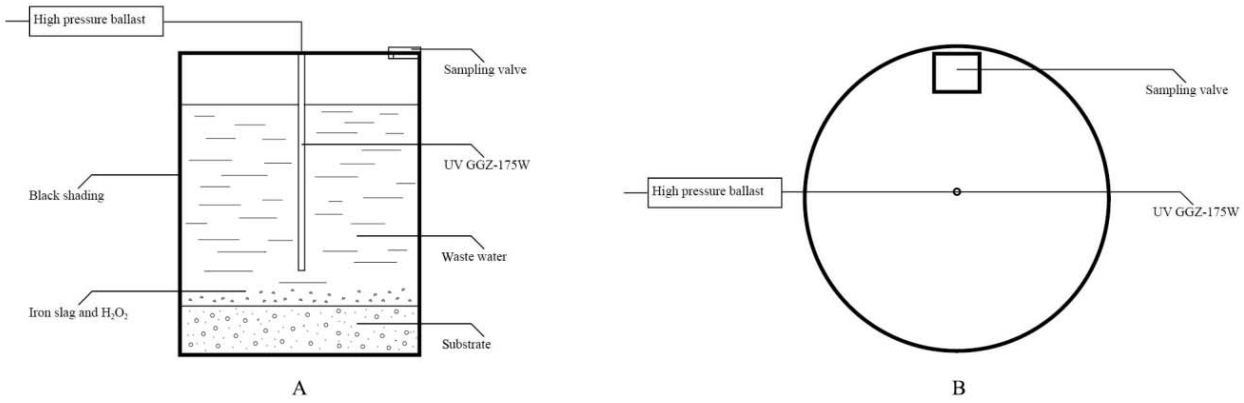

Fig. 1. Experimental device.

a movable sliding door on the top of the box to facilitate sampling during the experiment.

The reaction was carried out in a photocatalytic reactor, with 6 L wastewater disposed, and a certain amount of catalyst and H_2O_2 added. After the reaction in visible light, samples were taken at regular intervals for analysis.

Test Analysis

The filtered solutions were analyzed for residual Cr^{6+} concentration according to the 1,5-diphenylcarbazide method (detection limit of 0.02 mg/L Cr^{6+}) [26]. When the sample was collected, the pH of the sample was adjusted to 8 with 1 mol/L sodium hydroxide. All the obtained samples were centrifuged at 8000 r/min for 10 min on a high-speed centrifuge. Then using a 752 n UV vis spectrophotometer at 540 nm measure absorbance [28-29].

Statistical Analysis

The statistical analyses were performed using the Origin 8.0 statistical package (Origin Lab, USA). The data obtained were subjected to statistical treatment involving one-way analysis of variance. One-way ANOVA was used to analyze the difference of the orthogonal experiment. Differences were considered to be statistically significant at the 0.05 level, and a comparison of correlation coefficients (R) was performed.

Results and Discussion

Study on the Amount of Catalyst

The concentration of the catalyst has a significant effect on the reduction rate of Cr^{6+} in high-salt chromium-containing wastewater. Fig. 2 shows that, with the increase of a catalyst, the reduction rate of Cr^{6+} is significantly increased. When the catalyst concentration reaches 0.13 g/L, the reduction rate of Cr^{6+} reaches 99% and becomes stable, but the Cr^{6+} reduction rate decreases slightly, when the catalyst concentration is increased.

In the Fenton reaction, Fe^{2+} is a necessary condition to decompose ·OH from H_2O_2. The generation and production rate of ·OH become higher and higher with the increase of the Fe^{2+} concentration by the reaction (1). When Fe^{2+} is excessive, Fe^{2+} will be oxidized by the reaction with H_2O_2 (1), and the reaction between Fe^{3+} and H_2O_2 (2) will decrease the production of ·OH, which weakens the catalytic ability of the system.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2\cdot \quad (2)$$

Illumination Time and Reduction Rate

Cr^{6+} can be reduced by the catalyst under different light conditions. Fig. 3 shows that the reduction of hexavalent chromium can reach 99% for all three light sources by different reaction times. It takes 90 minutes for UV light, 270 minutes for sunlight and 540 minutes for dark environments.

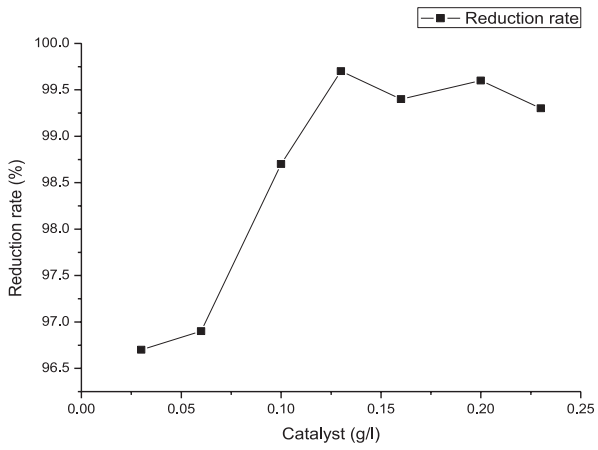

Fig. 2. Catalyst relative reduction rate of Cr^{6+}.

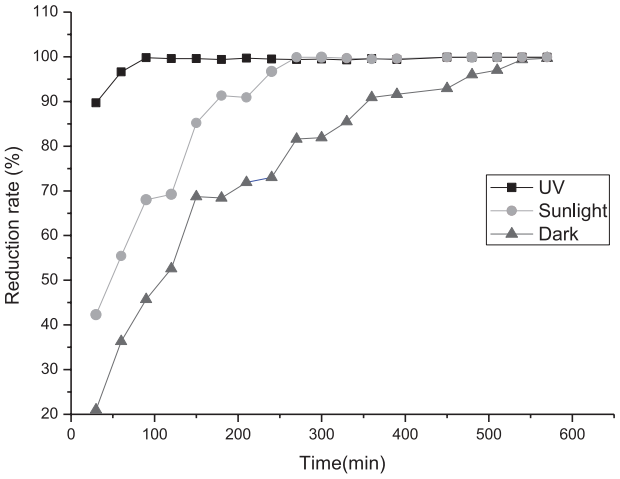

Fig. 3. Illumination time and reduction rate of Cr^{6+}.

The Fenton reaction in the dark environment utilizes the reaction between H_2O_2 and Fe^{2+} to produce ·OH (formula 1) to reduce hexavalent chromium. In homogeneous photocatalytic reaction, light and catalyst are synergistic [30-31], Fe^{3+} complexes can be directly reduced to Fe^{2+} by UV which reacts with H_2O_2 to produce· OH, which accelerates the reduction of Cr^{6+}. The rate of Fe^{3+}/Fe^{2+} is maintained in a good cycle under UV irradiation, and the utilization rate of the reagent can be increased to accelerate the reaction rate [32-33]. There is only 3-5% UV light in the sun, so the sun's reaction is slower than UV conduction. However, UV requires higher costs and it doesn't accord with the concept of ecological utilization. Considering the actual needs, and selecting sunlight to this study.

The Influence of Each Factor

pH

Fe^{2+} under acidic conditions can catalyze the production of ·OH from H_2O_2 in the Fenton reaction

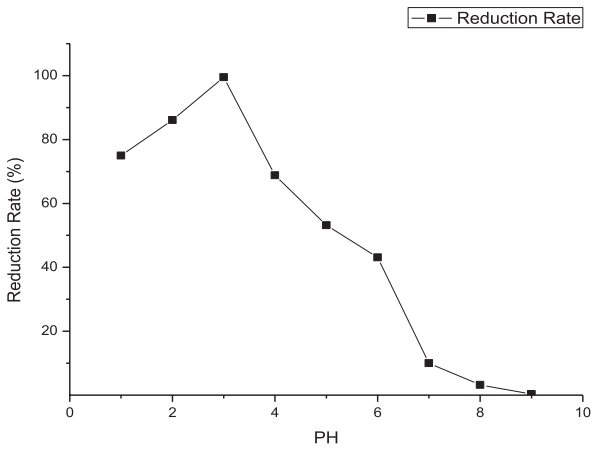

Fig. 4. pH and reduction rate of Cr^{6+}.

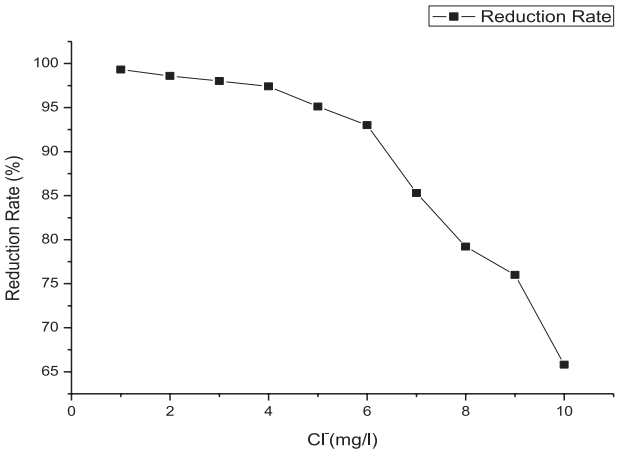

Fig. 5. Cl^- concentration and reduction rate of Cr^{6+}.

because the form of Fe^{2+} is controlled by pH [34]. The relationship between the reduction rate of hexavalent chromium and pH is shown in Fig. 4, and the reduction rate is the highest when pH value is 3. When the pH value is greater than 3, the reduction ratio of hexavalent chromium decreases with the increase of pH. When pH is greater than 7, the reduction rate of valence chromium is close to zero.

The pH value affects the balance of Fe^{2+} and Fe^{3+} directly, and thus affects the reduction effect of hexavalent chromium. When pH increases, Fe^{2+} exists as the hydroxide precipitate and loses its catalytic ability. If the concentration of H^+ in the solution is too high, reaction (2) will be inhibited.

Cl^- Concentration

The reduction ratio of hexavalent chromium comes down as the Cl^- concentration increases as shown in Fig. 5. When the Cl^- concentration is greater than 6 mg/L, the reduction of hexavalent chromium will be below 90%.

In the reaction system, the generated ·OH during the reaction not only oxidizes organic substances, but also consumes Fe^{2+} and H_2O_2 in the system, so the chain reaction is terminated [35-36]. In the reaction

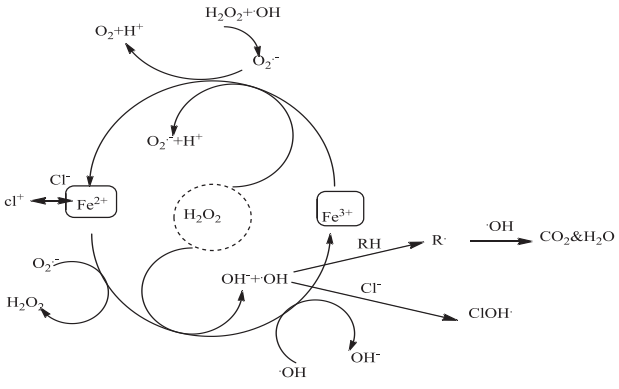

Fig. 6. Cl^- influence in reaction system.

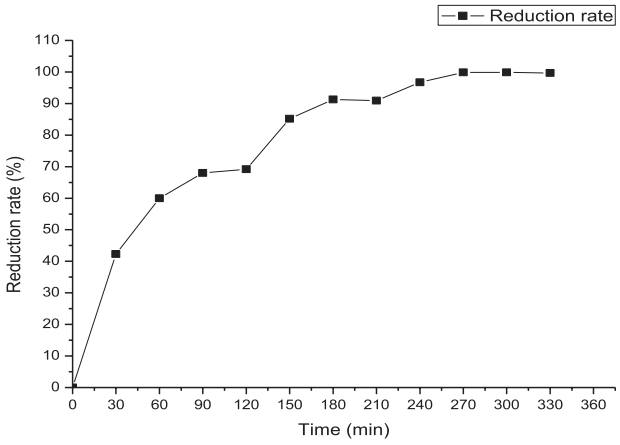

Fig. 7. The reaction time and reduction rate of Cr^{6+}.

Table 1. The orthogonal experiment factor variables.

Levels	Factors			
	pH	COD (mg/l)	Cl^- (mg/l)	Substance
1	3	50	5	Marble chips
2	6	100	8	Marble chips & Construction waste
3	9	150	10	Construction waste

system shown in Fig. 6, O_2^- in the reaction system not only oxidizes Fe^{2+} to Fe^{3+}, but also can reduce Fe^{3+} to Fe^{2+}, which plays a dual role in promoting and inhibiting the chain reaction [37]. The Cl^- in high-salt wastewater will consume a large amount of ·OH in the system and reduce the concentration of Fe^{2+} and Fe^{3+} by reaction. So the reduction ratio of hexavalent chromium is seriouly affected by the Cl^- the concentration [38-40].

Reaction Time

As shown in Fig. 7, the reduction rate of hexavalent chromium increases to 60% rapidly in 60 min, and after 60 min the reaction rate of hexavalent chromium gradually becomes slower. At the beginning of the reaction, a lot of H_2O_2 was consumed. As the reaction proceeds, the residual H_2O_2 concentration decreases and the reduction ratio of hexavalent chromium gradually decreases [41].

Orthogonal Experiment

In the experiment, four factors and three levels of orthogonal experiments were designed to determine the optimal conditions for treating wastewater. In this study, the four factors and three levels of orthogonality, including pH, COD, Cl^- concentration and substance as test factor variables, are shown in Table 1. Nine groups of tests were conducted totally. The experimental results are shown in Table 2.

Table 3 shows that the substance in the wetland has the smallest impact on the whole experiment, and pH has the greatest impact on the experiment, and then the COD and Cl^- concentration. The optimum experimental conditions were the following: pH value 3, COD concentration 100 mg/L, Cl^- concentration 5 mg/l, and substance is the marble chips and construction waste.

Reaction Mechanism of Fenton Reduction Cr^{6+}

The essence of the Fenton reaction is that Fe^{2+} reacts with H_2O_2 under strong acid conditions to form ·OH. The mechanism of Fenton reaction belongs to radical reaction. The reduction process of hexavalent chromium is under the irradiation of visible light, lattice iron in iron slag acts as a medium for electron transfer, and electrons can be transferred from the excited state to

Table 2. The orthogonal experiment experimental results.

Experiment NO.	Factors				Reduction rate of Cr(VI) (%)
	pH	COD (mg/l)	Cl^- (mg/l)	Substance	
1	3	50	5	Marble chips	95.2
2	3	100	8	Marble chips & Construction waste	85.5
3	3	150	10	Construction waste	79.6
4	6	150	5	Marble chips & Construction waste	45.5
5	6	100	8	Construction waste	43.6
6	6	50	10	Marble chips	33
7	9	100	5	Construction waste	0.5
8	9	150	8	Marble chips	1.8
9	9	50	10	Marble chips & Construction waste	1

Table 3. The orthogonal experiment range analysis results.

NO.	Range analysis results			
	pH	COD (mg/l)	Cl^- (mg/l)	Substance
k1	260.3	130	141.2	129.2
k2	122.1	132	130.9	129.6
k3	3.3	123.7	113.6	126.9
K1	86.8	43.3	47.1	43.1
K2	40.7	44	43.6	43.2
K3	1.1	41.2	37.8	42.3
R	85.7	2.8	9.3	0.9
Effects order	PH>Cl^->COD>Substance			
Excellent level	3	100	5	Marble chips & Construction waste

Cr^{6+} to simultaneously realize the reduction of Cr^{6+} [41], and it is proposed that the photoactive material can transfer electrons to Fe^{3+} to accelerate the decomposition of H_2O_2. The mechanism is shown in Equations 3-9.

$$\text{photoreactive species} + \text{visible light} \rightarrow \text{photoreactive species}^* + e^- \quad (3)$$

$$\equiv Fe^{3+} + e^- \rightarrow \equiv Fe^{2+} \quad (4)$$

$$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+} + {}^{\cdot}OH + OH^- \quad (5)$$

$$\equiv Fe^{3+} + H_2O_2 \rightarrow \equiv Fe^{2+} + O_2^{\cdot-}/HO_2^{\cdot} \quad (6)$$

$$\equiv Fe^{3+} + O_2^{\cdot-}/HO_2^{\cdot} \rightarrow \equiv Fe^{2+} + O_2 \quad (7)$$

$$\equiv Fe^{2+} + O_2^{\cdot-}/HO_2^{\cdot} \rightarrow \equiv Fe^{3+} + H_2O_2 \quad (8)$$

$${}^{\cdot}OH + \text{photoreactive species}^* \rightarrow \text{degraded products} \quad (9)$$

The main control step of the Fenton reagent participating reaction is the production of free radicals, especially·OH. There are a lot of the factors affecting the production of ·OH. During the reaction, Fe^{2+} and H_2O_2 will compete with organics for ·OH reaction and consume ·OH, which affects ·OH oxidation of organics. Therefore, pH, COD, Cl^-concentration of the wastewater, and the type and dosage of Fe^{2+} in the catalyst will all affect Fenton reaction about the treatment of wastewater.

Conclusions

The best conditions for chromium wastewater treatment of the homogeneous photocatalytic in constructed wetlands are as follows. The quantity of iron slag in the reaction was 0.13 g/L; pH value is 3; COD is 100 mg/L; Cl^- concentration is 5 mg/l; the reaction time is 270 min; and the sbustance is the stone and construction waste. In the reaction system, the influence of the factors follows the sequence: PH, Cl^-, COD and substance. pH was the main influencing factor. When the pH was 3, the reduced rate of Cr^{6+} could reach 99%. High salinity had a certain effect on Cr^{6+} reduction. When the Cl^- concentration was more than 6 mg/L, the Cr^{6+} reduction rate was below 90%.

The innovative point is the introduction of the photocatalytic method in common constructed wetlands, which not only reduces treatment costs but also meets the ecological concept of waste utilization. Owing to the high efficiency, low cost and cyclic utilization, it can be proposed that the iron slag could be used as an effective catalyst for Cr^{6+} removal in the photocatalytic constructed Wetlands.

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Conflict of Interest

The authors declare no conflict of interest.

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