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ORIGINAL ARTICLE

Photocatalytic Reduction of Cr(VI) from Aqueous Solutions with Formic Acid in the Presence of Bauxite: Kinetics and Mechanism

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Abstract Cr(VI) is one of the most dangerous heavy metal pollutants in the industrial wastewaters. It is very difficult to remove the Cr(VI) by direct precipitation and it is needed to be reduced to Cr(III) form in order to remove by conventional precipitation methods. The materials used in Cr(VI) reduction are SO_2 and its derivatives, Fe(II) salts and metallic iron. The reduction of Cr(VI)–Cr(III) is able to be achieved by a photocatalytic process. In this study, photocatalytic reduction of Cr(VI) in formic acid-bauxite system under irradiation by a medium-pressure mercury lamp (UV/visible) was investigated. Photocatalytic reduction of Cr(VI) over bauxite catalysts was investigated in both the absence and the presence of formic acid. Effects of initial pH value and formic acid initial concentration on Cr(VI) photocatalytic reduction were studied. The results indicate that formic acid-bauxite system is able to rapidly and effectively photocatalytically reduce Cr(VI) utilizing UV light. Initial pH variations are resulted in the changes of formic acid-bauxite in this system, and pH at 3.0 is optimal for Cr(VI) photocatalytic reduction. Kinetics analysis indicates that initial sulfuric acid and formic acid concentrations affects Cr(VI) photoreduction most significantly.

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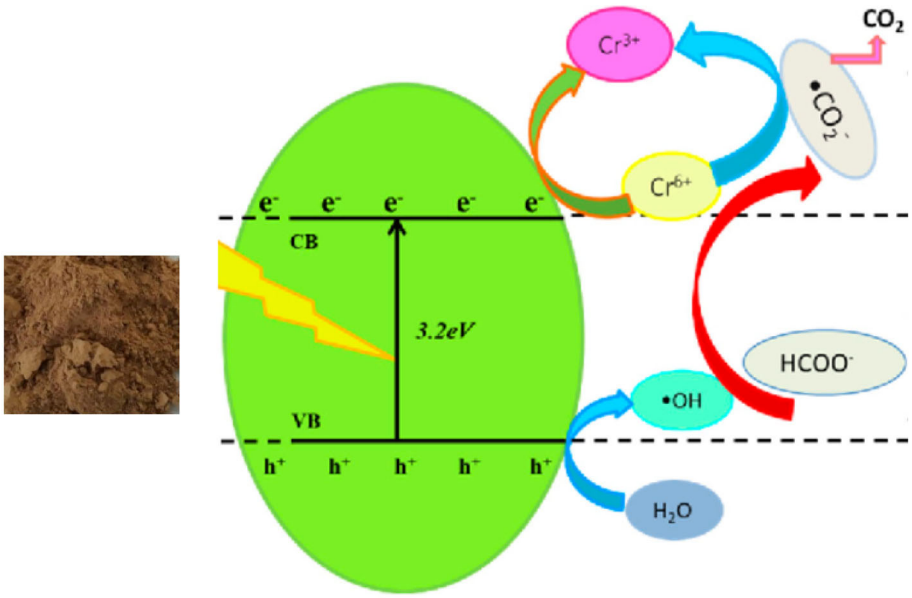
Graphic abstract



Keywords Photocatalyic reduction · UV · Cr(VI) reduction · Bauxite · Formic acid

1 Introduction

Water is a suitable solvent for most inorganic substances and some organic substances. Due to the fact that it is a carrier in terms of its cycle in nature, it can easily dissolve and absorb some of the substances it comes into contact with in the environments where water is used and transported. Some of the pollutants in the water degrade over time, their amounts in water and their effects accordingly decrease. However, some pollutants do not degrade at all and their amount in water increases. The most important of these types of pollutants are heavy metals. These are not eliminated in the aqueous environment and accumulate in sediments and realign under changing environmental conditions. These properties cause the continuation of its polluting and toxic properties in the environment. In order to prevent such effects, heavy metals must be removed from the water discharged into the environment by a suitable process [1].

The production and use of chromium itself and its compounds for industrial purposes, which is considered as one of the dangerous heavy metal pollutants in water, causes significant pollution. Chromium exists in the form of cationic Cr(III) and anionic Cr(VI) complex ions in aqueous medium. The toxicity of these two species is very different from each other. At the same time, Cr(VI), which is a strong oxidizer, has mutagenic and carcinogenic effects. Cr(III) is an essential element for animals up to certain amounts, and its toxic effect is much lower than Cr(VI) [1, 2].

The first step in classical Cr(VI) treatment is reduction to Cr(III), which is less toxic and can precipitate hydroxide. The remainder of the treatment consists of a precipitation and solid–liquid separation. Conventional reducers used to reduce Cr(VI)–Cr(III) in aqueous solutions are iron(II) sulfate, sulfur dioxide and sulfide compounds [3–5]. However, researches on this subject are continuing to determine the reduction agents with higher reduction efficiency, high ease of use, more advantageous and more economical in terms of forming secondary pollutants in aqueous medium. However, in these studies, it is seen that compounds containing iron and sulfur and various process residues have been investigated intensively as they are economical. In these studies, various parameters on the reduction of Cr(VI) in aqueous solutions were investigated in presence of steel wool [6], copper production reverber slag [7], iron ammonium alum [8], hydrated iron(II) sulfate [9], pyrite. Studies using materials such as [10], synthetic iron sulfide [11] and hydrogen sulfide [12] are examples.

Among the studies carried out in recent years, the possibilities of using organic materials as a reducing agent are also being investigated. Especially, the use of small molecules and organic substances that can turn into end products such as carbon dioxide and water without causing secondary pollution as a result of the reduction of Cr(VI) is seen as an important issue. As an example to these studies,

studies investigating the use of various monosaccharides [13] and various organic acids [14–17] as reducing materials can be given. However, since the reaction is relatively slow during the use of organic substances for reduction, it is generally carried out catalytically. The most common catalyst for this purpose is titanium dioxide. The possibilities of using TiO_2 in Cr(VI) reduction studies with the organic substances mentioned above have also been compared with some other metal oxide catalysts [17, 18].

Recently, developments have occurred in photocatalyst technologies. The result of this has also led to the use of photocatalyst technologies for water treatment. Today, the use of UV for water disinfection is quite common. In addition, there are researches on the use of UV radiation to remove toxic pollutants such as phenols from water by oxidation [18]. In a compilation study, it is stated that TiO_2 is at the head of the catalysts used for photocatalytic degradation of organic pollutants, and also WO_3, CdS, ZnS, SnO_2, WSe_2, Fe_2O_3, ZnO and TiO_2 with platinum and manganese have been investigated for these purposes [19].

Studies have been carried out to use UV radiation to reduce Cr(VI) in the presence of various catalysts, especially TiO_2 with the help of organic substances [20]. For example, one of these studies has focused on the measurement of chemical oxygen needs of wastewater by reducing Cr(VI) in the presence of UV/TiO_2 [21].

In this study, the possibilities of using formic acid to reduce Cr(VI) from aqueous solutions were investigated. The reason why formic acid is preferred as a reducing agent is that, it transforms into end products that do not have contaminating properties such as water and carbon dioxide while reducing Cr(VI). This is because, if organic substances with large molecules are used as reducers, small molecule organic materials formed during reduction may reduce the effectiveness of the next precipitation step by forming complexes with Cr(III). The studies have been carried out in a photocatalytic system, using bauxite as a solid catalyst, which is a raw material for aluminum production and contains some TiO_2 in its structure. Thus, the possibilities of using a reducing agent that does not cause a secondary pollution and an inexpensive catalyst obtained from nature to reduce Cr(VI) in the presence of UV have been investigated.

2 Materials and Methods

2.1 Bauxite's Supply, Preparation and Analysis

The bauxite sample used in the experiments was obtained from Etibank Seydişehir Aluminum Enterprises (Konya) during a doctoral study [22] conducted by us. The analysis results of the bauxite sample, whose chemical and mineralogical analyzes were carried out during the said doctoral study, are shown in Table 1, as well as physical and physicochemical properties in Table 2 [22]. Product morphology of the bauxite was observed by SEM (Fig. 1).

The crushed bauxite sample was ground in a disk mill and sieved through a 200 mesh (74 μm) sieve. The part remaining on the sieve was grinded again, and the whole sample was passed through 200 mesh. The ground and sieved sample was placed in metal pans and left to dry in an oven at 80 °C overnight. The dried bauxite sample was preserved in plastic containers with lids for use in experiments.

2.2 Preparation of Cr(VI) Solutions

In the experiments, the reduction of Cr(VI) with formic acid as bauxite catalytic and photocatalytic with UV was investigated. Therefore, stock Cr(VI), formic acid and sulfuric acid solutions were prepared before the preparation of the test solutions. Stock Cr(VI) solution at a concentration of 5000 mg/L was prepared by dissolving 14.14 g of $K_2Cr_2O_7$ salt in 1 L of distilled water. From this solution, intermediate stock solutions of 500 and 100 mg/L were prepared by gradual dilutions.

Stock formic acid (HCOOH) solution at 1.0 M concentration was prepared by taking 38.1 ml of 99% (1.22 g/cm^3) formic acid and diluting in 1 L of distilled water. The 1.0 M sulfuric acid solution was prepared by taking 55.5 ml of 96% (1.84 g/cm^3) solution and diluting it to 1 L volume with distilled water.

The Cr(VI) concentration of the solutions used in the reduction experiments conducted in the presence of UV was chosen as 10 mg/L (about 0.1 mM $Cr_2O_7^{2-}$). While preparing solutions at a concentration of 100 mg /L from stock Cr(VI) solutions, the stock formic acid and sulfuric

Table 1 Chemical and mineralogical compositions of bauxite [22]

Component	Weight (%)	Mineral	Weight (%)
Al_2O_3	56.91	Böhmit [AlOOH]	59.10
Fe_2O_3	16.95	Kaolinit [$Al_2Si_2O_5(OH)_4$]	11.34
SiO_2	8.62	Diaspor [AlO(OH)]	1.76
TiO_2	2.40	Hematite[α-Fe_2O_3]	15.39
CaO	0.91	Anatas [TiO_2]	1.49
CO_2	0.78	Calcite [$CaCO_3$]	1.29
P_2O_5	0.13	Quartz [SiO_2]	0.86
V_2O_5	0.03	Amorphous and Others	8.77
S	0.03		
Loss of ignition at 1100 °C	12.36		

Table 2 Some physical and physicochemical properties of bauxite [22]

Property	Value
Average particle size (μm)	18.54
Modal value (μm)	38.94
BET surface area (m^2/g)	11.0
Apparent density (g/cm^3)	1.4713
True density (g/cm^3)	2.1311
Porosity (cm^3/cm^3)	0.310
Average por diameter (μm)	3.689
PZNPC	8.39

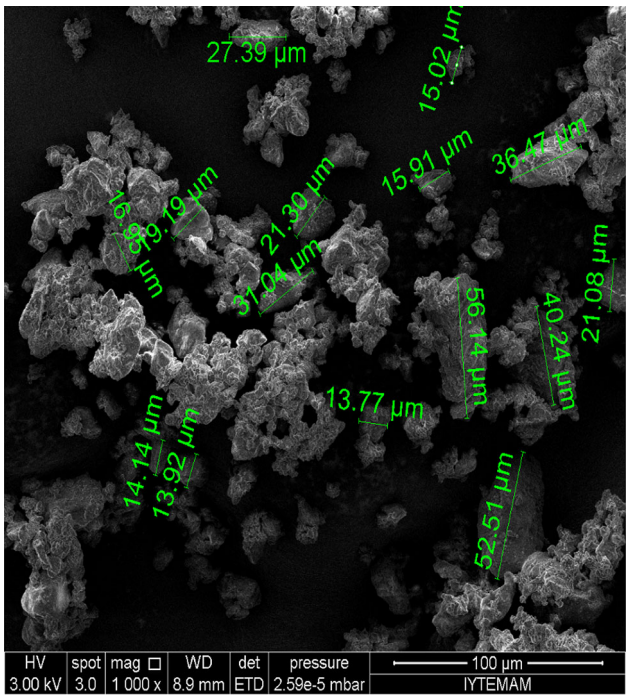


Fig. 1 SEM micrograph of a bauxite

acid solutions were added in moderate amounts, and the final volume was completed. Thus, test mixes were prepared in which the effect of formic acid and sulfuric acid amounts on reduction could be examined.

2.3 Experimental Study

The system in which photocatalytic reduction experiments were carried out is shown schematically in Fig. 2. The whole system was provided by Ace Glass (USA). As can be seen, the system is essentially a photocatalytic reactor made of 500-ml quartz glass containing the reaction mixture. This creates a quartz immersion well, which surrounds the UV lamp immersed in the reactor, preventing contact with the reaction mixture and at the same time preventing it from heating. The 450-W UV lamp placed in the immersion bowl is fed by a special power source. The UV lamp used is a low pressure monochromatic mercury vapor lamp. In addition, water is continuously circulated in the immersion container with the help of a thermostat-circulating water bath in order to prevent the lamp from overheating. A water flow sensor placed on the circulating water line transmits the received signal to a flow control unit. The flow control unit is connected to the inlet of the UV lamp supply unit, and in cases where there is no water flow, it automatically turns off the UV lamp supply unit to protect the lamp. In addition, the photocatalytic reactor system is placed in a closed cabinet to prevent direct contact with harmful UV rays. A magnetic stirrer is placed under the reactor to ensure constant speed mixing. In addition, at the upper part of the reactor, there are provisions for sample placement and removal temperature measurement and cooling water inlet and outlet. When the cover part of the cabinet used is opened, it is designed to cut the energy given to the whole system and to have a fan at the top of the cabinet to circulate the air inside.

With the experiments performed using this system and method, the effects of the amount of formic acid and the amount of sulfuric acid on the reduction efficiency were investigated with the UV-catalyzed Cr(VI) reduction experiments using formic acid and bauxite. In addition, experiments were made under certain conditions depending on the time and the reduction kinetics were tried to be determined.

In the photocatalytic reduction experiments, the system was started after filling the solution and bauxite mixture into the reactor. Afterward, samples were taken from the reaction mixture at regular intervals and filtered through a blue band filter paper. pH measurements, Cr(VI) and total Cr analysis were performed in these filtrates.

To meet the experimental conditions, 0.3 mM formic acid, 0.4-6.8 mM sulfuric acid and 8 g bauxite (20 g/L) were added to a 400 mL volume of 10 mg/L Cr(VI) solution, respectively. The effect of the amount of sulfuric acid as a result of reduction for 1 h was examined. After determining the most suitable acid amount range with these experiments, time-dependent experiments were carried out for the presence and absence of formic acid in this range. Then, time-dependent experiments were carried out by changing the formic acid concentration between 0 and 3.0 mM under the same conditions by selecting a certain sulfuric acid concentration.

2.4 Analysis of Solutions

Cr(VI) analysis in solutions was made according to the method of Diphenyl Carbazite [23]. The method is based on the spectrophotometric measurement of the colored

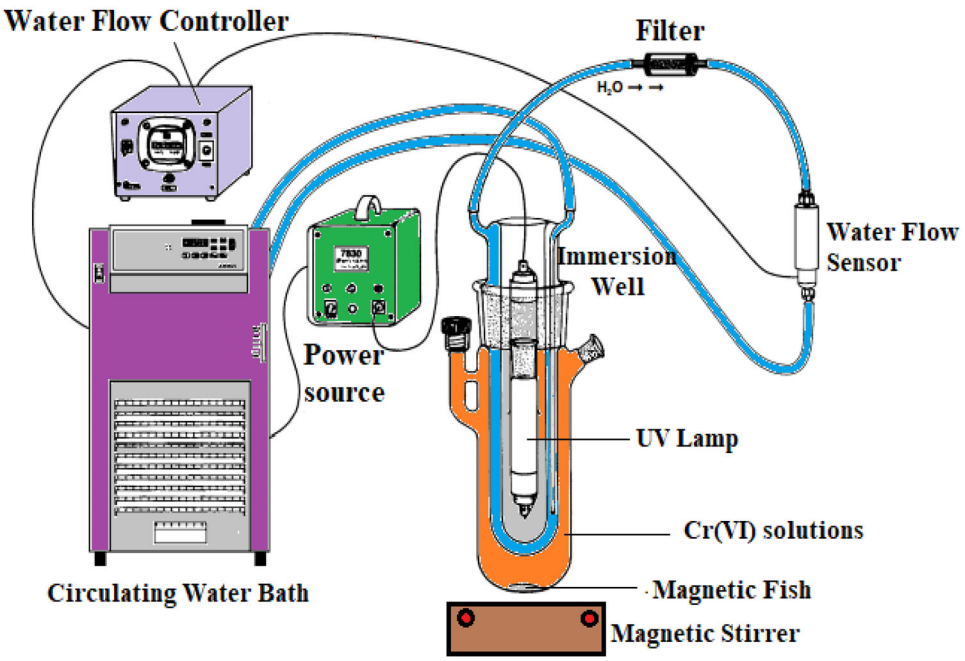


Fig. 2 Photocatalytic experimental system

complex formed by C(VI) with 1,5-Diphenyl Carbazite in an acidic medium. For this, Diphenylcarbazide solution obtained by dissolving 0.5 g of 1,5-Diphenylcarbazide in 100-mL acetone and 6 N H_2SO_4 solution were used as reagents. In the analysis of the Cr(VI) solution, 2 mL of 6 N H_2SO_4 and 1 mL of Diphenylcarbazide solution were placed in a 50 mL graduated flask. Thereupon, the appropriate amount of the solution to be determined was added and the absorbance at 540 nm wavelength was determined with a Schimadzu brand UV-1201 V model spectrophotometer and compared with the values of the standards. The total Cr analysis required for some samples was performed with an atomic absorption spectrophotometer (PerkinElmer AAnalyst 400). By comparing the absorbance values obtained for the standard solutions with the absorbance values obtained for the unknown samples, the concentration values of the unknown solutions were calculated by considering the dilution amounts.

3 Result and Discussion

In this study, the reduction of Cr(VI)–Cr(III), which is the first step of the reduction/precipitation process, which is the most common method used for the removal of Cr(VI) in aqueous solutions, was investigated photocatalytically. The possibilities of using formic acid as reducing agent and bauxite as catalyst were investigated. The method investigated in previous photocatalytic Cr(VI) reduction studies was the situation where TiO_2 was used as a catalyst in the presence of an organic reducer. It comes to mind that bauxite can be used as a catalyst because it contains various metal oxides as well as TiO_2. In addition, as a result of the oxidation of formic acid, end products such as carbon dioxide and water are formed. It is thought that these products have an advantage since organic complexing agents that prevent Cr(III) from being formed as a result of reduction are not formed in the medium. Based on these ideas, this study has been carried out to investigate the reduction of Cr(VI) with formic acid in aqueous solution with UV presence and bauxite catalysis. When $K_2Cr_2O_7$ is in solution, it acts as an acceptor of photocatalytically generated electrons, and the concentration of Cr(VI) decreases by reducing it to Cr(III). The reactions are expressed as follows [21].

In these mechanisms, both e^- reactions and h^+ reactions produce oxygenated reagent species that can be oxidized. This often causes organic structures to break down through oxidation. However, it should not be forgotten that when there is a type that can take e-against the electron in the conductivity layer, it causes reduction by electron transfer. Therefore, TiO_2 is like a bidirectional machine and can perform both oxidation and reduction simultaneously. Although the production of oxidizing species is much higher, h^+ production is also proportional to the consumption of electrons in the conductivity band. It should not be forgotten that the more h^+ or e^- is consumed (by oxidation or reduction) TiO_2 will regenerate these species. Therefore, organic species can be added to the medium, for example to enhance the reduction pathway.

$$TiO_2 + h\nu \rightarrow h^+ + e^- \quad (1)$$

$$h^+ + H_2O \rightarrow {}^{\cdot}OH + H^+ \quad (2)$$

$${}^{\cdot}OH + R \rightarrow \text{Degradation of organic matter} \rightarrow CO_2 + H_2O \quad (3)$$

$$h^+ + R \rightarrow \text{Degradation of organic matter} \rightarrow CO_2 + H_2O \quad (4)$$

$$2Cr_2O_7^{2-} + 28\ H^+ + 12e^- \rightarrow 4Cr^{3+} + 14H_2O \quad (5)$$

$$28\ H^+ + 2CrO_4^{2-} + 6\ e^- \rightarrow 4Cr^{3+} + 8H_2O \quad (6)$$

$$Cr_2O_7^{2-} + 3HCOOH + 8\ H^+ \rightarrow 2\ Cr^{3+} + 3\ CO_2 + 7H_2O \quad (7)$$

However, due to the use of bauxite as a catalyst in the medium, it may be possible to remove some Cr(VI) by adsorbing to the bauxite surface. For this reason, total Cr concentrations as well as Cr(VI) concentrations were determined in the experiments. Equation 7 shows that 3 mol of formic acid and 4 mol of sulfuric acid are needed per 1 mol of $Cr_2O_7^{2-}$ due to reaction stoichiometry. Therefore, initially, experiments were carried out with solutions containing sulfuric acid at concentrations ranging from 0.4 to 6.8 (1–17 times the stoichiometric amount) in addition to 10 mg/L Cr(VI) (0.1 mM $Cr_2O_7^{2-}$) and 0.3 mM formic acid in the presence of UV and bauxite. Thus, the effects of sulfuric acid amount and hence pH on reduction efficiency were investigated. Under these conditions, the reduction and adsorption efficiencies and pH values observed at the end of a reaction time of 60 min are collectively shown in Fig. 3. As can be seen from the figure, the reduction efficiency increases with increasing sulfuric acid concentration. For example, while the reduction efficiency of Cr(VI) obtained with acid at a concentration of 0.4 mM (stoichiometric amount) is 11.4%, almost all of the Cr(VI) is reduced at a concentration of 6.0 mM (15 times the stoichiometric amount).

As can be seen from Fig. 3, a part of Cr(VI) is adsorbed on bauxite surface. The amount of Cr(VI) removed by absorption depends heavily on ambient acidity. While the amount of Cr(VI) adsorbed at high pH is low, it first increases a little with the decrease in pH and then decreases again. It can be said that this situation is caused by the change in the pH and surface loads of bauxite and the change in the reduced Cr(VI) amounts depending on the pH. It is stated in previous studies that the net zero proton load (pHzpc) point for bauxite is 8.39 [24]. This means that above pH value, the surface is partially negatively charged and partially positively charged below it. Therefore, around this pH value, the amount of negative and positive charges on the surface is close to each other. As the pH decreases,

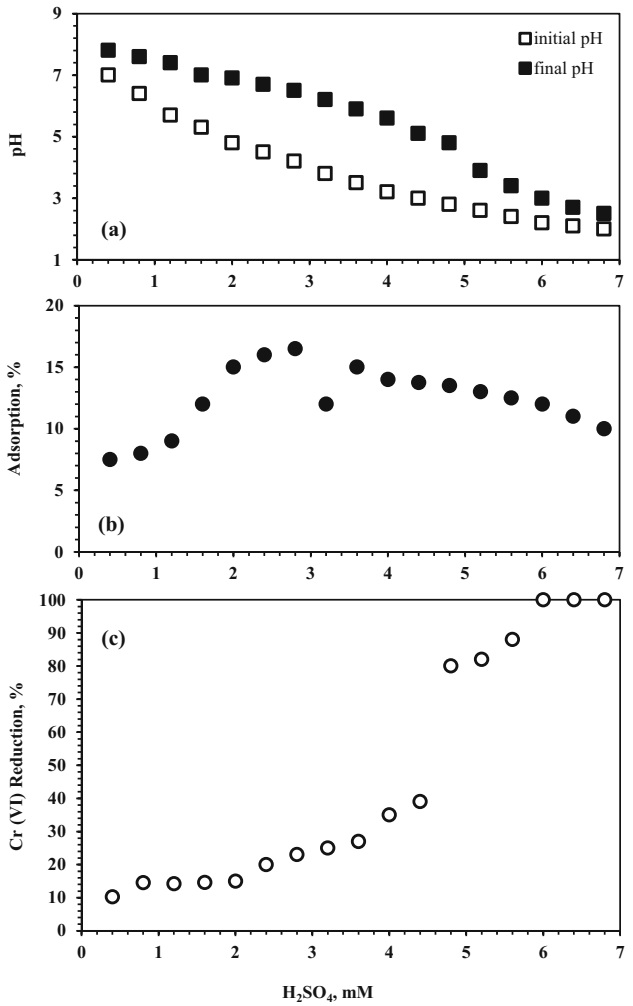


Fig. 3 Effect of H_2SO_4 concentration on the reduction of Cr(VI) in the presence of formic acid. **a** pH_{final}; **b** Cr(VI) adsorption; **c** Cr(VI) reduction. [Cr(VI) starting conc.: 10 mg/L; formic acid conc.: 0.3 mM; bauxite dosage: 20 g/L; reaction time: 60 min.]

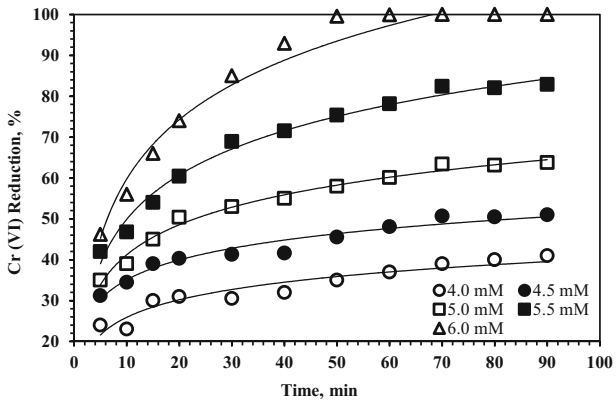


Fig. 4 Cr(VI) reduction yields based on time of H_2SO_4 concentration to Cr(VI) reduction in the presence of formic acid. (Initial Cr(VI) concentration: 10 mg/L; bauxite dosage: 20 g/L; formic acid concentration: 0.3 mM]

the surface becomes positively charged and becomes suitable for adsorbing negatively charged Cr(VI) species. On the other hand, since the decrease in pH also increases the Cr(VI) reduction rate, the adsorption of positively charged Cr(III) formed this time will be difficult on positively charged surfaces. Therefore, it is expected that the adsorption will decrease due to the increase in the adsorption of Cr(VI) first with increasing acidity and then the increase in the amount of Cr(III). Finally, it can be thought that the lower initial pHs than the final pH of the mixture are due to the basic materials in bauxite structure.

In the range of 4.0–6.0 mM, where the effect of sulfuric acid concentration on the Cr(VI) reduction rate is significant, experiments were carried out depending on the time. The effect of sulfuric acid concentration on Cr(VI) reduction rate can be seen in Fig. 4. As can be seen from the figure, the reduction rate increases significantly with increasing sulfuric acid concentration. At the end of a 90 min contact time, reduction efficiencies for 4.0, 4.5 and 5.0 mM H_2SO_4 concentrations are around 41%, 51% and 63%, respectively. For 5.5 mM H_2SO_4, this value is around 84% in 80 min, and for 6.0 mM H_2SO_4, all of the Cr(VI) reduce to Cr(III) within 60 min.

The test results obtained depending on the time can be evaluated in terms of kinetics. Although there are events such as Cr(VI) adsorption, formic acid adsorption, surface reactions of adsorbed species accompanying the reduction event, the kinetics of the event can be examined by considering the change in Cr(VI) concentration. In previous similar studies, a first order kinetic model, expressed as follows, is proposed [14].

$$-\frac{\mathrm{d}[\mathrm{Cr(VI)}]}{\mathrm{d}t} = \mathrm{k_{obs}}[\mathrm{Cr(VI)}] \tag{8}$$

here the symbol [Cr(VI)] represents the concentration, k_{obs}, the observed first order rate constant, and t represents the time. If the equation is integrated by writing it as a transformation fraction, it takes the following form:

$$-\ln(1-X) = \mathrm{k_{obs}}t \tag{9}$$

where X represents the conversion fraction, and the Cr(VI) can be found by dividing the reduction yields by 100. As you can see, equation is a line equation, and it is obtained by plotting the values of t against $-\ln(1-X)$. The slope of the line will be equal to the apparent velocity constant (k_{obs}). The model graphs drawn as a result of applying the time-dependent removal efficiencies obtained for different H_2SO_4 concentrations to the first order kinetic model are shown in Fig. 5. Apparent velocity constants and correlation coefficients calculated from the slope of the model lines obtained for different sulfuric acid concentrations are shown in Table 3. As can be seen from the table, the speed increases significantly with increasing acid concentration in the range studied [25]. The rate of reduction observed at 6.0 mM H_2SO_4 concentration is approximately 37 times the rate observed at 4.0 mM.

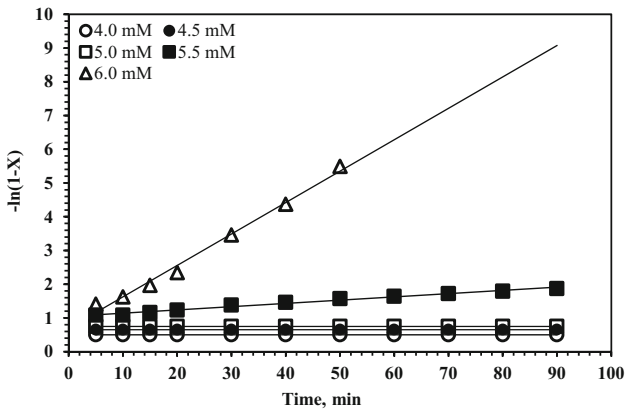


Fig. 5 Application of time-dependent Cr(VI) reduction yields for different H_2SO_4 initial concentrations to the first order kinetic model. [Initial Cr(VI) concentration: 10 mg/L; bauxite dosage: 20 g/L; formic acid concentrations: 0.3 mM stoichiometric]

Table 3 Rate constants and correlation coefficients calculated for different sulfuric acid concentrations

H_2SO_4		
mM	k_{obs}, dk^{-1}	R^2
4.0	0.0028	0.960
4.5	0.0039	0.970
5.0	0.0070	0.979
5.5	0.0203	0.985
6.0	0.1040	0.985

In order to investigate the effects of formic acid concentration on reduction kinetics, time-dependent reduction experiments were carried out with solutions containing formic acid at concentrations varying between 0 and 3.0 mM as well as 10 mg/L Cr(VI) and 6.0 mM H_2SO_4. The results obtained are shown in Fig. 6. As expected, the Cr(VI) reduction rate increases with increasing formic acid concentration [26]. For example, the time required for the reduction of all Cr(VI) is 60 min for 0.3 mM formic acid concentration, while this time is around 20 min for 3.0 mM concentration. The main point to be mentioned is that, the whole Cr(VI) is reduced at the end of a period of 60 min even in the absence of formic acid in the medium. This situation is thought to be caused by organic substances in bauxite. Because during the geological formation of bauxite deposits, it is possible that they coexist with organic based fossil layers. For this reason, during the production of alumina with the Bayer process, a pre-calcination or burning process can be applied to remove organic substances before basic digestion.

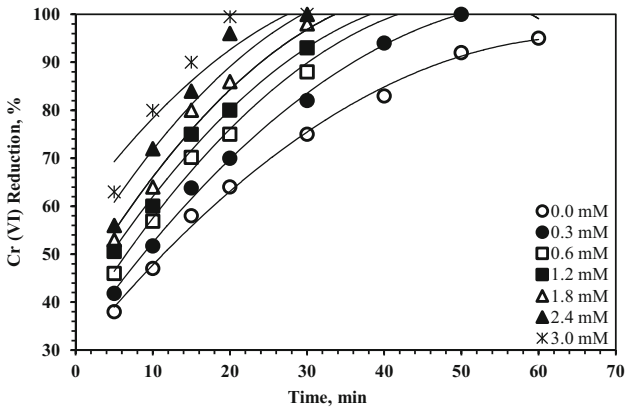


Fig. 6 Cr(VI) reduction efficiencies obtained depending on time for different initial formic acid concentrations. [Initial Cr(VI) concentration: 10 mg/L; bauxite dosage: 20 g/L; sulfuric acid concentration: 6.0 mM]

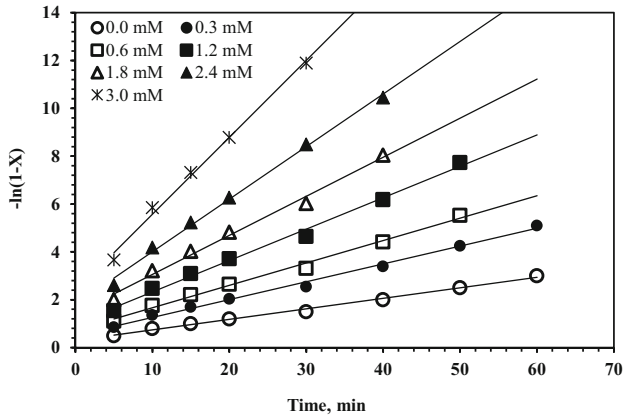


Fig. 7 Application of Cr(VI) reduction yields obtained with time for different initial formic acid concentrations to the first order kinetic model. [Initial Cr(VI) concentration: 10 mg/L; H_2SO_4 concentration: 6.0 mM; bauxite dosage: 20 g/L]

Experimental data obtained depending on the time for different starting formic acid concentrations were also applied to the first order kinetic model. The obtained model lines are shown in Fig. 7, and the first order velocity constants and correlation coefficients calculated from the slope of the lines are shown in Tables 4, 5. It is seen that the experimental data obtained fit very well to the first order kinetic model. On the other hand, the increase in the reduction rate with increasing formic acid concentration can be understood from the values of the determined rate constants [24–26]. When the rate constant value observed for 0.3 mM (approximately 1 stoichiometric amount) formic acid concentration is compared with the rate constant for 3.0 mM concentration, it is seen that the rate constant increases approximately 3.5 times although the formic acid concentration increases 10 times. In addition, compared to the situation where there is no formic acid in the medium, it is seen that the speed increases approximately 8 times.

Table 4 Rate constants and correlation coefficients calculated for different formic acid concentrations

HCOOH		
mM	k_{obs}, dk^{-1}	R^2
0.0	0.048	0.986
0.3	0.104	0.985
0.6	0.113	0.983
1.2	0.132	0.990
1.8	0.178	0.977
2.4	0.217	0.991
3.0	0.381	0.973

Initial Cr(VI) concentration: 10 mg/l; H_2SO_4 concentration: 6.0 mM; bauxite dosage: 20 g/l

Table 5 Rate constants and correlation coefficients calculated for different initial sulfuric acid concentrations

H_2SO_4		
mM	k_{obs}, dk^{-1}	R^2
4.0	0.0045	0.951
4.5	0.0150	0.979
5.0	0.0237	0.994
5.5	0.0370	0.999
6.0	0.0480	0.986

Initial Cr(VI) concentration: 10 mg/L; bauxite dosage: 20 g/L; H_2SO_4 concentrations: 4.0, 4.5, 5.0, 5.5 and 6.0 mM stoichiometric; formic acid concentration: 0

As can be seen from these results, it can be said that organic substances in bauxite have an important reducing effect. For this reason, a series of experiments have been carried out to investigate the amount of acid, which is the most important parameter that can affect the reduction rate of Cr(VI), with bauxite and UV without using formic acid. The effect of time on reduction efficiency at a dose of 20 g /L bauxite from Cr(VI) solutions at concentrations of 10 mg/L was investigated in the 4.0–6.0 mM H_2SO_4 concentration range. The results obtained are shown in Fig. 8. As can be seen from the figure, the amount of reduced Cr(VI) increases with increasing sulfuric acid concentration and time. At the end of 60 min, the reduction efficiency obtained at 4.0 mM acid concentration is 39.2%, while this value is 95.3% for 6.0 mM concentration. These results show that it is possible to reduce Cr(VI) in the presence of UV with organic substances in bauxite. Here, too, the data obtained depending on the time have been applied to the first order kinetic model. The model graphics obtained are shown in Fig. 9 and the velocity constants and correlation coefficients calculated from the slope of the

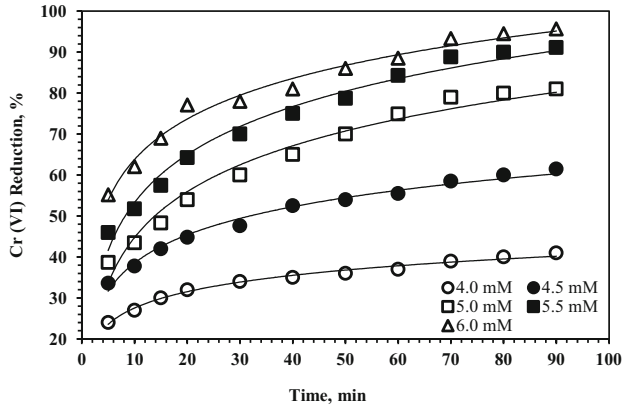


Fig. 8 Cr(VI) reduction efficiencies obtained with time for different initial sulfuric acid concentrations. (Initial Cr(VI) concentration: 10 mg/L; bauxite dosage: 20 g/L; H_2SO_4 concentrations: 4.0, 4.5, 5.0, 5.5 and 6.0 mM; formic acid concentration: 0)]

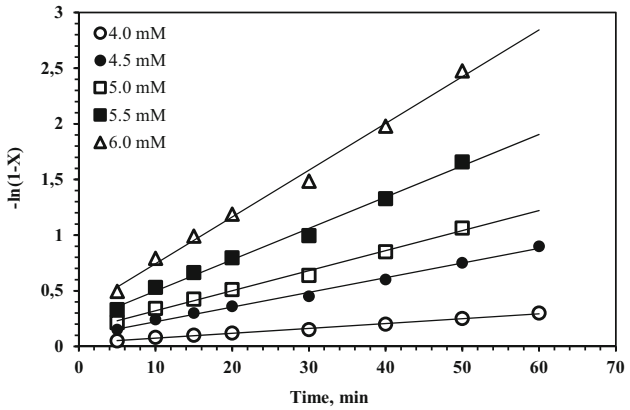


Fig. 9 Application of Cr(VI) reduction yields obtained with time for different initial sulfuric acid concentrations to the first order kinetic model. [Initial Cr(VI) concentration: 10 mg/L; bauxite dosage: 20 g/L; H_2SO_4 concentrations: 4.0, 4.5, 5.0, 5.5 and 6.0 mM stoichiometric; formic acid concentration: 0]

lines are shown in Table 6. As can be seen from the table, in the absence of formic acid, the Cr(VI) reduction efficiency of organic substances in bauxite is significantly dependent on the sulfuric acid concentration. The rate constant value determined for 6.0 mM acid concentration is approximately 10 times the rate constant determined for 4.0 mM acid concentration [25, 26]. It is clear from this result that the rate increases more with increasing sulfuric acid concentration in the presence of formic acid compared to the situation in the absence of formic acid.

4 Conclusion

In order to reduce Cr(VI) in aqueous solution to C(III), which is less toxic and can be removed by a hydroxide precipitation, photocatalytic method was performed using reducing formic acid, UV as a method and bauxite as a catalyst.

Bauxite can be considered as a catalyst for photocatalytic processes since it contains around 2.5% TiO_2, which is one of the leading semiconductors commonly used in photocatalytic processes. In addition, bauxite contains other metal oxides other than TiO_2 that may show catalytic effects.

As it is a heterogeneous system, the Cr(VI) in the medium as well as the Cr(III) are formed as a result of the reduction affect in the reduction process performed in aqueous solution using the UV/bauxite system. It can also be said that the events such as the adsorption of formic acid and the consumption of the added sulfuric acid by the basic oxide components to ensure sufficient acidity for reduction accompany the reduction event. Because the total Cr analysis and pH measurements made confirm this situation.

Experiments investigating the effect of 10 mg/L concentration Cr(VI) as well as sulfuric acid amount on

Table 6 Comparative performance of typical photocatalysts for Cr(VI) reduction

Photocatalysts	Experimental conditions						Reduction efficiency (%)	References
	pH	Dose (mg)	Volume (mL)	Concentration (mg/L)	Time (min)	Light source		
MIL-68(In)-NH_2	2.0	40	40	20	180	300-W Xe lamp (> 420 nm)	97	[27]
CuS@MIL-125	2.1	25	50	48	70	500-W Xe lamp (> 420 nm)	52	[28]
Bi2S3 nanosphere	2.0	20	40	40	120	500-W Xe lamp (> 420 nm)	90	[29]
p-NiO@n-Nb2O5	2.0	50	50	58	300	500-W Tungsten lamp	100	[30]
Cu2O@BiVO4	–	50	100	9	120	300-W Xe lamp (> 420 nm)	100	[31]
g-C3N4@GO@BiFeO3	2.0	500	200	5	120	300-W Xe lamp (> 400 nm)	100	[32]
WO3@MIL-53(Fe)	2.5	20	100	45	240	Sunlight	94	[33]
Bauxite	2.0	20	200	10	60	450 W UV (low-pressure monochromatic mercury vapor lamp)lamp	100	This work

reduction from solution containing formic acid in stoichiometric ratio have shown that the easily observable reduction range is 4.0–6.0 mM H_2SO_4 concentration. It has been determined that the reduction is very slow at concentrations below this and very fast above this range. The results of the reduction experiments conducted in this interval depending on the time have been applied to the simple first order kinetic model and it is determined that the reduction rate increases approximately 37 times by increasing the H_2SO_4 concentration from the calculated rate constants from 4.0 to 6.0 mM.

As a result of the experiments conducted with solutions containing 0.0–3.0 mM formic acid in addition to 10 mg/L Cr(VI) (about 0.1 mM $Cr_2O_7^{2-}$) and 6.0 mM H_2SO_4 in order to examine the effect of formic acid concentration on the reduction kinetics, it is seen that the reaction rate increases approximately 35 times when the amount of formic acid is increased to 10 times the stoichiometric amount. Therefore, it can be said that sulfuric acid has more effect on speed than formic acid.

The reduction experiments conducted with solutions that do not contain formic acid show that it is possible to reduce Cr(VI) in significant proportions. This situation is thought to be caused by organic substances in bauxite. It also explains that the reduction activity depends more on the concentration of sulfuric acid than on the concentration of formic acid.

Experiments examining the effects of sulfuric acid concentration on Cr(VI) reduction without formic acid show that increasing sulfuric acid concentration increases the rate of reduction significantly. By increasing the H_2SO_4 concentration from 4.0 to 6.0 mM, the reduction efficiency increases approximately 10 times.

Additionally, the photocatalytic performance of Cr(VI) removal between bauxite and the other photocatalysts reported in recent years has also been compared as shown in Table 6. The results reveal that bauxite act as photocatalyst with excellent performance for Cr(VI) reduction.

As a result, it can be said that it is possible to reduce Cr(VI) in a photocatalytic system where bauxite is used as a catalyst. In addition to providing the reduction process by organic substances in bauxite, it is possible to add reducing organics to the medium. The use of formic acid for this purpose is considered advantageous, in that it turns into end products that do not have polluting properties such as carbon dioxide and water after reduction.

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