Reduction of noxious Cr(VI) ion to Cr(III) ion in aqueous solutions using H₂O₂ and UV/H₂O₂ systems

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A B S T R A C T

Conversion of the toxic Cr(VI) to the less toxic Cr(III) in aqueous solutions by chemical and photochemical reduction was carried out using H₂O₂ and UV radiation. The whole mechanism was well elucidated and investigated using potassium dichromate (K₂Cr₂O₇) as a standard model compound. The effects of potential factors affecting the reduction efficiency were well studied and optimized, the optimized parameters such as concentration of H₂O₂ (from 0.5 to 1.5 M), pH (from 5 to 9), irradiation time (0 to 140 min) and reaction time (0 to 120 min). Initial concentration of Cr(VI) in the solution was varied from 0.1 to 15 mg/L plays a significant role in the mechanism involves for the reduction of noxious Cr(VI) to less toxic Cr(III).

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Chromium occurs in the nature mainly in three common oxidation states, i.e. Cr(III) and Cr(VI) and Cr(0), the former being the most stable form and available naturally in the environment while the latter are generated due to several hazardous industrial processes [1]. Cr(VI) ion is noxious to most of the biotic organisms as well abiotic organisms, higher than 0.05 ppm concentration of Cr(VI) lead to severe detrimental and lethal effect on the prevailing flora and fauna [2], it act as carcinogenic agent in animals and causes severe irritation problems in humans. Cr(VI) ion is very soluble in water and forms divalent oxy-anions such as CrO₂⁻ and dichromate (Cr₂O₇²⁻). As it is a sorbent, Cr(VI) ion can easily flow through sediments and cause contamination of aquifers, groundwater and various other forms of aquatic source. Cr(III) is readily precipitated or adsorbed on a variety of inorganic and organic substrates at neutral or alkaline pH [2,3]. Reduction of noxious Cr(VI) to stable Cr(III) plays a vital role in the remediation of environmental sites contaminated by chromium. Indeed, Cr(III) is an essential nutrient (especially in glucose metabolism) for all the biotic creatures including flora as well as fauna [2–4], on the other hand Cr(VI) is perilous to humans, animals, plants and microorganisms and lead to severe detrimental effect on the liver and kidney, causes internal hemorrhage, dermatitis, respiratory damages and lung cancer [2–5]. According to the World Health Organization (WHO), the metals which are required to remove from the environment and need immediate concern are Cr, Zn, Fe, Hg and Pb [6]. The maximum allowed limits for contaminants in “treated” wastewater are enforced in developed and many developing countries [3,4]. Several techniques and adsorbents such as electrocoagulation [7], activated carbon from lignin seeds [8], zeolite prepared from raw fly ash [9], exfoliated polypyrrole-organically modified montmorillonite clay nanocomposite [10], illuminated ZnO/TiO₂ composite [11], alumina [12] were used for the sorption and reduction of the Cr(VI) species.

In the presented work, the rapid reduction of Cr(VI) ion by UV, H₂O₂ and UV/H₂O₂ was well studied and elucidated using K₂Cr₂O₇ solutions as a model contaminant. The impact of the crucial parameters such as irradiation time with UV, concentration of H₂O₂, pH, initial concentration of Cr(VI) ion and reaction time were well examined and optimized. Hydrogen peroxide has been used as

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the reduction reagent. H$_2$O$_2$ is both not toxic and effective and it converts to O$_2$ and H$_2$O in the reaction with Cr(VI) ion. The purpose of this study was to investigate the reduction of Cr(VI) ion in aqueous solutions using H$_2$O$_2$ and UV/H$_2$O$_2$ systems.

**Materials**

Analytical grade (AR) reagents were purchased from different suppliers and were used without any further purification. Potassium dichromate (K$_2$Cr$_2$O$_7$) was used as the model solution for the production of Cr(VI) ion. Hydrogen peroxide (H$_2$O$_2$) solutions 2% (30%, v/v) were prepared by dilution of 30% H$_2$O$_2$ (Merck) in double distilled water.

**Experimental**

The experiments were carried out in a cylindrical glass reactor with 12 cm in inner diameter and 30 cm in height (Fig. 1). A 1000-mL Cr(VI) ion solution (adjusted at different physiological pHs according to the experiment) was introduced into the reactor with a predetermined amount of H$_2$O$_2$. The reactor was tightly closed and the reaction solution was stirred by means of a magnetic stirrer to ensure complete mixing. For the photo reduction experiments, an ultraviolet lamp fixed at 254 nm and 8 W power) was attached into a quartz glass tube at the center of the reactor. Samples were withdrawn at different time intervals and analyzed to monitor the progress of the reaction. The reactor temperature was maintained constant at 20 ± 1°C by circulating chilled water.

The residual concentrations of Cr(VI) ions were measured spectroscopically in a Perkin–Elmer Lambda 25 UV–vis Spectrophotometer (Perkin–Elmer, Norwalk, CT) by the diphenylcarbazide method at 540 nm [13]. Cr(VI) ion reduction was calculated and expressed in percentage.

The results of the rapid reduction of Cr(VI) ion by H$_2$O$_2$ per time are presented in Fig. 2. The reduction rate of Cr(VI) ion was very fast initially, leading to a rapid decrease in the concentration of Cr(VI) ion. About 86, 74 and 64% of the initial Cr(VI) ion was reduced within the first 5 min of reaction at different physiological pHs 5, 7 and 9, respectively. Then, the residual concentration of Cr(VI) ion became almost constant after 15 min of reaction time. Therefore, subsequent experiments were performed at this reaction time.

Fig. 3 shows a linear relationship between the logarithm of the Cr(VI) ions concentration and the reaction time, showing that the reduction of Cr(VI) ions by H$_2$O$_2$ followed first-order kinetics. The relationship between the reduction efficiency of Cr(VI) ion and the pH value is shown in Fig. 4. It reveals that the pH had a significant effect on the reduction of Cr(VI) ion using H$_2$O$_2$. Reduction of Cr(VI) ion in acidic and neutral solutions by hydrogen peroxide was more efficient than in alkaline solution. In general, the pH value of surface water and groundwater is between 5 and 9. Most of the reduction reagents reported in the literature was either less effective or non-effective in alkaline solutions [2–4,14]. However, H$_2$O$_2$ reduced Cr(VI) ion in a wide range of pH.

In the physiological pH range from 1 to 6, HCrO$_4^–$ is the predominant form of Cr(VI) ion, while above pH 6 the anion CrO$_4^{2–}$ predominates [2]. As shown in Fig. 4 the pH value had a significant effect on the reduction of Cr(VI) ion. Thus, increasing the pH from 5 to 9 at an initial concentration of 0.1 mg/L of Cr(VI) ion, the percentage of reduction decreased from 83.0 to 54.8% (Fig. 4).

The reduction of Cr(VI) followed first-order kinetics:

\[ \ln \frac{C}{C_0} = k_{\text{red}} t \]

where $k_{\text{red}}$ is the photo catalytic reduction rate constant, $t$ is the reaction time, $C$ is the concentration of Cr(VI) ion at time zero and $C$ is the Cr(VI) ion concentration at a particular time. The observed first-order rate constants for the decrease in the concentration of Cr(VI) ion as a function of pH, are presented in Table 1, reveals that the pH of the reaction solution has a significant effect on the
shows the values (\([\text{Cr(VI)}]\) reduction 1.5 Fig. 3. Plot of \(\ln(C/C_0)\) vs time for the reduction of \(\text{Cr(VI)}\) by \(\text{H}_2\text{O}_2\) at different pH values (\([\text{Cr(VI)}]\) 0.5 mg/L; \([\text{H}_2\text{O}_2]\) 1.5 M).

Fig. 2. Effect of the reaction time on the reduction of \(\text{Cr(VI)}\) by \(\text{H}_2\text{O}_2\) at different pH values (\([\text{Cr(VI)}]\) 0.5 mg/L; \([\text{H}_2\text{O}_2]\) 1.5 M).

Fig. 3. Plot of \(\ln(C/C_0)\) vs time for the reduction of \(\text{Cr(VI)}\) by \(\text{H}_2\text{O}_2\) at different pH values (\([\text{Cr(VI)}]\) 0.5 mg/L; \([\text{H}_2\text{O}_2]\) 1.5 M). Reduction rate. Thus, the reduction rate increased with decrease in the pH of the solution.

In the reduction of \(\text{Cr(VI)}\) ion to \(\text{Cr(III)}\) ion by \(\text{H}_2\text{O}_2\), the reduction of \(\text{Cr(VI)}\) ion depends on the \(\text{H}_2\text{O}_2\) concentration. Fig. 5 shows the relationship between the reduction yield of \(\text{Cr(VI)}\) ion and the \(\text{H}_2\text{O}_2\) concentration. The major species of Cr at pH < 6 is \(\text{HCrO}_4^-\). Therefore, the molar amount of \(\text{H}_2\text{O}_2\) required for the reduction of \(\text{Cr(VI)}\) ion concentration can be obtained from the following stoichiometric equations:

\[
2\text{HCrO}_4^- + 3\text{H}_2\text{O}_2 + 8\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{O}_2 + 8\text{H}_2\text{O} \tag{2}
\]

\[
\text{Cr(VI)} + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow 3\text{Cr(III)} + \text{H}_2\text{O} + \text{O}_2 \tag{3}
\]

Despite the high oxidation ability of \(\text{H}_2\text{O}_2\), it acts as a reductant (\(E = 0.678\) V) in the presence of stronger oxidants such as chlorine (\(\text{Cl}^-\) \(E = 1.77\) V), potassium permanganate (\(\text{KMnO}_4\) \(E = 1.52\) V) and \(\text{K}_2\text{Cr}_2\text{O}_7\) \(E = 1.33\) V). However, for the effective reduction of \(\text{Cr(VI)}\) especially at high pH large quantities of \(\text{H}_2\text{O}_2\) are required [5].

The effect of UV/\(\text{H}_2\text{O}_2\) at different physiological pH and initial \(\text{Cr(VI)}\) ion concentrations and different irradiation times was investigated. As shown in Fig. 6, the reduction efficiency decreased with increasing initial concentration of \(\text{Cr(VI)}\) ion and irradiation time. As in the case of the use of \(\text{H}_2\text{O}_2\) alone, the \(\text{H}_2\text{O}_2\) concentration had an acute effect on the reduction of \(\text{Cr(VI)}\) to \(\text{Cr(III)}\) by using UV/\(\text{H}_2\text{O}_2\).

Within 15 min irradiation, the removal efficiency of UV/\(\text{H}_2\text{O}_2\) was less than that obtained when only \(\text{H}_2\text{O}_2\) is used as reductant. This can probably be attributed to the thermodynamic instability of \(\text{H}_2\text{O}_2\), which decomposes in \(\text{H}_2\text{O}\) and \(\text{O}_2\) at high temperature [3].

\[
2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2, \Delta H = -99\text{ kJ/mol} \tag{4}
\]

With the increase in the UV irradiation time the decomposition of \(\text{H}_2\text{O}_2\) becomes higher so that and it was found that at pH 9 and 60 min of reaction time the reduction efficiency of \(\text{Cr(VI)}\) ion was zero. As mentioned in the previous section, \(\text{H}_2\text{O}_2\) is a strong oxidizer that can act as a reducer in the presence of stronger oxidants [1,3,15].

\[
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}, E_0 = 1.77\text{ V} \tag{5}
\]

Table 1

<table>
<thead>
<tr>
<th>pH</th>
<th>(k_{\text{red}}) (min(^{-1}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
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<td>0.9696</td>
</tr>
<tr>
<td>7</td>
<td>0.01738</td>
<td>0.9906</td>
</tr>
<tr>
<td>9</td>
<td>0.01335</td>
<td>0.9924</td>
</tr>
</tbody>
</table>

Fig. 4. Effect of pH on the reduction of \(\text{Cr(VI)}\) by \(\text{H}_2\text{O}_2\) ([\(\text{Cr(VI)}\)] 0.5 mg/L; [\(\text{H}_2\text{O}_2]\) 1.5 M), reaction time 15 min.

Fig. 5. Effect of the \(\text{H}_2\text{O}_2\) concentration on the reduction of \(\text{Cr(VI)}\) by \(\text{H}_2\text{O}_2\) at different [\(\text{Cr(VI)}\)] (pH 5, reaction time 15 min).
Xu et al. [13] also studied the reduction of Cr(VI) ion, but using ascorbic acid, it was observed that in the presence of UV reduction of Cr(VI) ion increased with the decreasing pH, increasing ascorbic acid concentration, and increased reaction time [2].

To explore the effect of UV (UV radiation—1020 μW/cm²) on the reduction of Cr(VI) ion, experiments were conducted at different physiological pHs range from 5 to 9, concentrations of Cr(VI) ion (from 0.1 to 15 mg/L) and irradiation times (from 15 to 60). It was found that the effect of UV alone on the reduction of Cr(VI) ion to Cr(III) ion was negligible.

The initial concentration of Cr(VI) ion in the drinking water samples was 0.077 mg/L. The wastewater used in this study was collected from the effluent of a metal plating plant. The wastewater was characterized in terms of pH, conductivity and Cr(VI) ions.

The residual concentrations of Cr(VI) ions after the treatment by H₂O₂ and UV/H₂O₂ reached much lower values than the maximum acceptable concentration (MAC) in drinking water (MAC = 0.5 mg/L) according to USEPA [16]. Therefore, the present study revealed that water treatment using H₂O₂ can decrease the concentration of Cr(VI) ion from both drinking water and industrial wastewater, in addition, this method can be used at municipal scale in water treatment plants. Real drinking water samples (i.e. tap water) were collected and the application of reaction agents, namely H₂O₂, UV/H₂O₂ and UV, for the rapid reduction of Cr(VI) to Cr(III) were carried out. The maximum reduction carried out by the reagents was found to be 92%, at the optimized initial pH of 5, a reaction time of 15 min and at 1.5 M initial H₂O₂ concentration. The results indicated that H₂O₂ was effective in the remediation of Cr(VI) contaminated water in a wide physiological range of pH, either with or without UV.

Photocatalytic removal and reduction of Cr(VI) with UV/H₂O₂ was compared with other reports in the viewpoint of removal efficiency, contact time in Table 2. This comparison shows that the UV/H₂O₂ is an effective catalyst for the reduction of Cr(VI) from aqueous solution compared to UV and H₂O₂ alone. The reasonable reason for the enhanced removal of Cr(VI) observed in the UV/H₂O₂ may be due to the mechanism involved in electron transfer as well as a hole transfer from the valence band [12, 17–22].

In conclusion reduction of Cr(VI) ions from the aqueous solutions by H₂O₂, H₂O₂/UV and UV as redactants using K₂Cr₂O₇ solution as a model contaminant was well studied and elucidated. The concentration of H₂O₂ had a crucial effect on the reduction of noxious Cr(VI) ion, the concentration of H₂O₂ and the reaction time required for the reduction of Cr(VI) ion was higher in alkaline than that in acidic conditions and, thus, the reduction efficiency increased with the decreasing pHs. On the other hand for the commercialization of this process, this treatment was applied to real samples and the results showed that the residual concentrations of Cr(VI) ions in the samples after the treatment by H₂O₂ or UV/H₂O₂ reached to lower values than the maximum acceptable concentration in drinking water.

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**References**


![Graph](image.png)