The study progress and application of dithionite reduction technology in the treatment of environmental pollutants

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Abstract. Environmental pollution has seriously influenced the human health and ecological security. As a strong reducing agent, dithionite has been gradually drawing the attention of researchers and engineers in the environmental field. Studies had been conducted by employing dithionite to treat the pollutants such as halogenated organic compounds, oxyacid salts, and heavy metals. However, few works were focusing on the dithionite reduction, especially the dithionite detection. This report aimed to review the characteristic of dithionite including the chemical properties and detection methods. The research progressing on the treatment of environmental pollutants by the reactive species generated from dithionite was also summarised. However, ultraviolet seemed to be the only choice of the dithionite activation methods, no matter what pollutant was to be degraded. Accordingly, the research, on the development of dithionite detection and activation methods, was prospected.

1. Introduction

Environmental pollution, caused by industrial and agricultural activities, has seriously influenced the quality of life and eco-system in the past several decades [1]. Various environmental pollution problems was led by different industries due to their diverse processes and products such as refractory halogenated organics generated from organic chemical industry [2], heavy metal pollutants from mining and electroplating industry [3], and high-valent oxyacid salts, for example nitrates, produced in human life [4] etc. Hence, it is a great challenge to remove the various toxic pollutants effectively [5]. Several emerging pollutants have high potential toxicity to living organisms and are a great concern to the ecosystems, for example, the typical halogenated organic pollutants (perfluorocarboxylic acids, pesticides, personal cares (PPCPs) and pharmaceuticals), toxic inorganic pollutants including metal ions etc. It is urgent and necessary to degrade these pollutants effectively. However, it is difficult to remove the typical refractory organics using the traditional treatment (bio-oxidation, adsorption, coagulation and sedimentation etc) [6].

Concerning on the environmental and human safety, more attention has been paid on applying the advanced reduction processes (ARPs), which are based on the redox potential, for the pollution remediation. The reactive free radicals generated from the redox reactions have the ability to remove pollutants normally. The sulfur-containing chemicals have widely applied in pollution control by means of the diverse redox characteristic, especially in the soil and ground water remediation. Among these chemicals, dithionite was the most selected one as the reducing agent to repair the land contaminated by chlorinated organic pollutants [7]. It is promising for dithionite to apply in ARPs to
treat wastewater in aquifers and other environmental remediation application depending on the practicality and effectiveness in the pollution control [8]. However, there were few reports or reviews on the generalization about the research progress and prospect of dithionite even in the field of environment. In this review, the characteristic and research progress of dithionite was addressed. The chemical properties, detection methods, and the application of the dithionite reduction technology on wastewater treatment and environmental remediation were reviewed. Finally, the new research priorities and application of dithionite were stated.

2. Characters of dithionite
Dithionite or hydrosulfite (S$_2$O$_4^{2-}$) is a strong reducing agent and of great industrial significance, commonly known as insurance powder. It was named by the special chemical bond of S-S between the two SO$_2^-$ [9]. It always has two different forms of dihydrate and anhydrous salt. The dihydrate salt is a slight yellow flaky crystal, which is extremely unstable in nature and only exists in the alkaline solution. The dihydrate salt will be dehydrated and converted into the anhydrous one when being heated to a certain temperature. In addition, the anhydrous salt is a white crystalline powder and is unstable in the drying state at room temperature. The structural formula of dithionite is shown in Figure 1.

![Figure 1. The structural formula of dithionite.](image)

2.1. Chemical properties
Though dithionite is commonly known as insurance powder, dithionite is an unstable chemical with the highly reactivity. Dithionite can decompose to release heat and easily cause the combustion after absorbing moisture. And when heating up to above 75 °C, dithionite may release heat and generate the toxic and flammable sulfur dioxide (Eq. 1 and 2).

\[
2\text{Na}_2\text{S}_2\text{O}_4 \xrightarrow{\Delta} \text{Na}_2\text{S}_2\text{O}_3 + \text{Na}_2\text{SO}_3 + \text{SO}_2
\]

\[
2\text{Na}_2\text{S}_2\text{O}_4 \xrightarrow{\Delta} \text{Na}_2\text{S}_2\text{O}_3 + \text{S} + \text{SO}_2
\]

Dithionite can be oxidized to bisulfite (HSO$_3^-$) and hydrogen sulfate (HSO$_4^-$) when exposing to air (Eq. 3). Moreover, it will cause a severe redox reaction releasing a large amount of heat and toxic substances when combined with the oxidizing acid, such as sulfuric acid, perchloric acid, nitric acid, and phosphoric acid etc (Eq. 4).

\[
2\text{Na}_2\text{S}_2\text{O}_4 + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{NaHSO}_3 + \text{NaHSO}_4
\]

\[
2\text{S}_2\text{O}_4^{2-} + 4\text{H}^+ \rightarrow \text{S}_\downarrow + \text{SO}_2 \uparrow + 2\text{H}_2\text{O}
\]

It can be seen that the Gibbs free energy ($\Delta G$) of dithionite is located between sulfurous and thiosulfuric according to the $\Delta G$ corresponding to the different oxidation states of sulfur (Figure 2) [10]. In addition, the redox of dithionite is about -1.12 V so that it has the great potential to form the ARPs [11].
2.2. Environmental application
Dithionite has been widely used in pollution control due to the low cost, reactive properties, and low toxicity. The dithionite is widely applied for the removal of heavy metal and organic pollutants in groundwater. The most common applications focus on the dehalogenation of halogen organic, reduction of high-valence oxyacid salt (e.g. ClO$_3^-$, NO$_3^-$ etc.) and heavy metal etc. Except for the environmental application, dithionite also can be applied in the chemical industry such as printing, dyeing, and food handling. It can be served as the reagent of dyeing, cleaning, and bleaching, especially for the wood pulp paper.

2.3. Detection methods
It is significant for the detection of dithionite to explore the transformation rules in the process of dithionite reduction technology. The accurate and convenient detection methods have not been explored because of its instability nature [12]. However, the strong reducing and special fluorescent properties can be employed for the novel detection development. Several researchers have established the methods of oxygen absorption, iodometric, anaerobic fluorescence titration, and capillary electrophoresis etc. based on the above principles. We have concluded the following methods which have drawn attention to several researchers in the field of pollution control.

2.3.1. Iodometric. Currently, iodometric is considered to be the most popular and precise method to adapt to the demand of various studies. According to the chemical industry standard, the solution prepared by the quantitative sample and the neutral formaldehyde solution is titrated by iodine standard solution with the starch indicator to determine titration endpoint. Then the effective content of dithionite can be indirectly computed by the consumption of iodine standard solution indirectly. The process can be briefly described as that dithionite can react with the neutral formaldehyde solution to generate bisulfite formaldehyde and hyposulfite formaldehyde, and then hyposulfite formaldehyde will consume the same amount iodine (Eq. 5 and 6).

\[
\text{Na}_2\text{S}_2\text{O}_3 + 2\text{CH}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{NaHSO}_3 \cdot \text{CH}_2\text{O} + \text{NaHSO}_2 \cdot \text{CH}_2\text{O} \quad (5)
\]

\[
\text{NaHSO}_2 \cdot \text{CH}_2\text{O} + 2\text{I}_2 + 2\text{H}_2\text{O} \rightarrow \text{NaHSO}_4 + \text{CH}_2\text{O} + 2\text{HI} \quad (6)
\]
2.3.2. Anaerobic fluorescence titration. The fluorescence can provide the proper application in the detection of dithionite. Anatol et al [13] have described the process in details. Briefly speaking, two sealed culture tubes were prepared in the anaerobic condition containing a certain concentration of flavin mononucleotide (FMN) and dithionite, respectively; then a quantitative FMN was extracted with a pre-deoxidized polytetrafluoroethylene syringe; finally, they were inserted into another tube containing dithionite to react with FMN to generate FMNH₂ (Eq. 7).

\[ \text{S}_2\text{O}_4^{2-} + \text{FMN} + 2\text{H}_2\text{O} \rightarrow \text{FMNH}_2^+ + 2\text{HSO}_3^- \]  

(7)

The reaction endpoint can be determined by the disappearance of fluorescence because FMN can emit fluorescence under ultraviolet radiation while FMNH₂ show no fluorescence. So the concentration of dithionite can be calculated by the variety in the quality of the tube containing dithionite. Obviously, this method can be used in the detection of dithionite in biochemical research.

2.3.3. Other detection methods and the prospect. The titration methods have no special demand on the experiment apparatus so that it always serves as the most popular method in the detection. However, it may be affected by the difference in operation and determination of titration endpoint. So the development of a novel detection method acts as a research items to adapt to the different research purpose. For example, only the rough detection results are required in the practical pilot, so the colorimetric method may be satisfied for the demand of engineering commissioning. Moreover, related patents have introduced the detection method of oxygen absorption based on the consumption of oxygen by dithionite in a confined reactor. It suggests that it is significant and valuable to develop novel methods for dithionite detection to adapt on the different reaction systems.

3. Application of pollutants treatment

Due to the strong reducing ability of dithionite, it is effectively to remove the contaminants with the oxidizing property. The traditional application focuses on the chemical reducing of heavy metal and halogenated organic. However, the exploration related to the novel ARPs has been paid more attention due to the increasing recognition and understanding on ARPs.

3.1. Dehalogenation

Halogenated Organic Compounds (HOCs) refer to organic compounds having one or more halogen atoms in the organic structure, such as perfluorinated compounds (PFCs), triclosan, haloacetic acid (HAAs), and trihalomethanes (THMs) and so on. At present, the toxicity and high stability of HOCs have gained widespread attention all over the world. It is challenging and attractive for the researchers to solve the environmental pollution generated by HOCs. The biodegradability of HOCs can be obviously improved via the dehalogenation by dithionite. Garcia et al [14] had studied the enhancement of 1,2-dichloroethane by dithionite with the nano-zerovalent iron (nZVI) in the soil remediation by reducing reaction. The results showed that the apparent first-order reaction rate constant can be increased from 3.8×10⁻³ d⁻¹ to 7.8×10⁻³ d⁻¹ after the enhancement of nZVI and the final products have been confirmed as FeS or FeS₂. In addition, the similar researches have been conducted by Rajasekar et al [15]. They have also explored that the degradation rate of trichloroethylene could be increased by 40 times via dechlorination combined dithionite with the vulcanized nZVI. Besides, the application of UV-activated dithionite ARP is still the most widely studied for the degradation of HOCs. Liu et al [16] had studied the dechlorination of 1,2-dichloroethane (1,2-DCA) by dithionite, sulfite, sulfide, and Fe²⁺ activated by UV, respectively. The results showed that dithionite and sulfate had similar performance, and 1,2-DCA could be completely degraded within 100 min under alkaline and neutral conditions. It indicates that it is important for the treatment of HOCs for the selected reducing agents. It could also have about 50% degradation capacity even under acidic condition. Furthermore, Hara et al [17] also had explored the degradation of 2,4,6-trichlorophenol by UV/dithionite under the different wavelengths of UV. They had discovered that dithionite could be
activated by short-wave ultraviolet (UV-C) at the maximum extent at pH 9~10 while vacuum ultraviolet (V-UV) had no excitation effect on dithionite.

3.2. Reduction of oxyacid-salt

Several oxyacid-salts such as dichromate, arsenate, chlorate, and nitrate etc. can be converted into the nontoxic or low-toxic substances by dithionite reducing in the environment. Chlorate (ClO$_3^-$), served as a common inorganic disinfection by-product (DBP) in drinking water, has caused widespread concern for the human health and ecological security. Some researchers have gradually taken dithionite into consideration for the control of DBPs. Jung et al [18] had applied the system of UV/dithionite to control the concentration of ClO$_3^-$. It had revealed that a wavelength of 312 nm had the best influence on the activation of dithionite. Besides, there were two degradation steps of the degradation of ClO$_3^-$. Firstly, the products of dithionite decomposition caused the rapid degradation of ClO$_3^-$ before the irradiation. Secondly, the products of dithionite decomposition could be induced by dithionite to generate free radicals which could react with ClO$_3^-$ to product Cl$^-$. In addition, nitrate (NO$_3^-$), a more ubiquitous environmental contamination, has the significant impact on the environment and always serves as the important target pollutant for environment control. Except for the biochemical methods, many researchers also attempted to remove it by ARPs. In fact, it is feasible for NO$_3^-$ to be reduced by dithionite in theory and practice. Bensalah et al [19] had studied the removal of NO$_3^-$ by hydration electrons (e$_{aq}$) generated from activated dithionite under medium-wave ultraviolet (UV-M) radiation. It revealed that NO$_3^-$ had the obvious and rapid degradation under a neutral or alkaline condition with the main degradation mechanisms of direct photolysis, direct chemical reduction of dithionite, and reduction radical reduction. And the final products included nitrite, ammonia, and released nitrogen.

3.3. Reduction of heavy metal

When treating soil and water environment by heavy metal, there are several kinds of pollutants cannot be removed by traditional chemical precipitation directly. So it is necessary to add the pre-treatment to improve the treatability and make it able to be precipitated. Coincidentally, dithionite can act as the proper reducing agent to pre-treat these heavy metals. Chromium, arsenic, and copper were the most studied one.

Su et al [20] had conducted the study on the ecological remediation of chromium-containing soil with dithionite and examined the bioavailability of chromium based on the gastrointestinal simulation method in the soil. It was found that the bioavailability of hexavalent chromium had greatly decreased about 63.21%~84.67% after the remediation of dithionite and reduced the health risks of it effectively. Also, combination ferrous with dithionite was used to conduct the in-situ remediation of chromium-containing groundwater by Ludwig et al [21]. The remediation process mainly utilized the reduction and adsorption of Fe$^{2+}$ to convert hexavalent chromium into trivalent. The addition of dithionite could prolong the continuous remediation of chromium-containing groundwater.

Apart from the studies on the soil and groundwater environment contaminated by chromium, plenty of works also have performed on the different environmental media contaminated by selenium, arsenic and copper to minimize the hazard to human life and ecosystems. Jung et al [22] had attempted to treat the Se(IV)-containing wastewater by UV/dithionite. The soluble Se(IV) could be completely degraded at the range of lower pH in the system of UV/dithionite. Besides the decomposition product of dithionite could also degrade the soluble Se(IV) in dark condition. Similarly, Kaushik et al [23] had conducted the study on the removal of As(V)-containing wastewater based on UV-activated dithionite. The better removal of As(V) with the apparent reaction rate reaching 616 L/(mol·min) at around pH 6.0 was achieved. It was also revealed that the soluble contaminations had been converted into the low toxicity products. The reasonable explanation could be concluded that there was a large amount of hydration electrons (e$_{aq}$) generated from the process of dithionite activated by UV.

As to copper-containing wastewater, many researchers had also sought the appropriate approach to transform it into the other state. Chou et al [24, 25] had conducted the chemical reduction of Cu$^{2+}$ and the result revealed that dithionite could transform the different complexed Cu$^{2+}$ into the low valence copper including zero-valent copper.
3.4. Prospect of environmental application of dithionite

At present, the environmental applications based on dithionite is aimed for the wastewater treatment, soil and groundwater remediation because the reducibility of dithionite has confirmed to the current pollution situation. So it has great potential to develop the novel and effective ARPs to enhance the ability to reduce the pollutants. Besides, most of the studies focus on the chemical reduction and ultraviolet advanced reduction processes to remove HOCs, oxyacid salts, and heavy metal. So it is significant for us to explore whether there are any other effective for dithionite activation to develop the novel ARPs. The oxidizing substance may have the feasibility to activate dithionite due to the possibility to generate the reactive species when combined it with dithionite. So developing the creative systems of dithionite has the better prospect of application.

4. Conclusion

Dithionite has gradually grabbed more attention to the degradation of contaminations in the wastewater treatment and remediation of soil and groundwater due to the strong reducibility. The review has concluded the characteristic of dithionite involved the chemical prosperities, environment application, and detection methods. Iodometric is the most popular method for the detection of dithionite but with the disadvantage of inconvenient of operation and difficulty to control.

The widely application of dithionite focus on the reduction of HOCs, oxyacid salts, and heavy metals etc. While ultraviolet is the simplest and effective activation method of dithionite to generate some reactive species for the removal of pollutants. Overall, there are several feasible study directions on dithionite in the environmental application. Our future research has been focused on the spectrophotometry derived from iodimetry and the homogeneous activation methods to dithionite to make it more applicable and valuable in the field of pollution controlling.

5. References

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