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Preparation of Various Types of Ferrates: A Review

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Abstract**-- Ferrates are strong oxidising agents which are obtained by oxidation of iron (III) into iron (VI). Ferrate (VI) has the potential to be used as an environmentally friendly treatment for waste water and drinking water. Ferrate is the most powerful, multipurpose, environmentally friendly water and wastewater purification chemicals known. In a single dose, super-charged iron(VI) replaces multiple treatment chemicals because it can simultaneously disinfect, oxidize and coagulate to remove pathogens and contaminants from water. Ferrate destroys human pathogens, including viruses, spores, bacteria and protozoa. It can remove or inactivate toxic metals, pesticides, drugs, hormones and industrial toxins found in drinking water, wastewater, ballast water, municipal and industrial effluents, tainted soils and groundwater. Unlike chlorine and ozone, which produce harmful by-products, ferrate's by-product is an environmentally friendly insoluble iron(III) species. Hence synthesis of ferrate is much more important. Various types of ferrates are potassium ferrate, sodium ferrate, cesium ferrate, rubidium ferrate, barium ferrate, strontium ferrate, silver ferrate etc. An alkali metal ferrate can be converted into an alkaline earth metal ferrate.**

Keywords**--ferrate(VI), preparation, oxidant, applications, chemical stability, ferrate(VI) salts, water treatment.**

I. INTRODUCTION

Ferrates are chemical compounds containing iron in the exceptionally high oxidation state of +6. The ferrates show strong oxidising power hence useful as water treatment agents, for treating waste water and as cathodes in alkaline batteries. Ferrate(VI) in comparison with other current oxidants is a cheap and low-risk one. (1)

Ferrates were reported for the first time in 1841 by Fremy and were then described by Stahl in 1884. The electrochemical preparation of ferrate can be considered a "green" and simple approach because it typically involves a one-step reaction without harmful or expensive chemicals for the oxidation of Fe(0) to Fe(VI). The persulphate is indifferently used in sodium form ($Na_2S_2O_8$), potassium form ($K_2S_2O_8$) or ammonium form ($(NH_4)_2S_2O_8$). It is commercially available in sodium and potassium form. In general, the amount of persulphate is in a stoichiometric excess of about 1 to 15% with respect to the amount of iron (III) compound. Potash (KOH) is generally commercially available as pellets; it is used in a stoichiometric excess of about 0.5 to about 10% with respect to the amount of iron(III) compound.

The method of the invention makes use of persulphate, which is a stable compound which is not very toxic and has a good oxidizing power. The reaction can be represented in the following way:

$$10KOH + Fe_2O_3 + 3K_2S_2O_8 \rightarrow 2K_2FeO_4 + 6K_2SO_4 + 5H_2O$$

II. DIFFERENT WAYS OF FERRATE GENERATION

Fe(VI) salts are obtained by reaction of a solution of soda and calcium hypochlorite with an Fe(III) salt such as $Fe(NO_3)_3$. Another method which is relates to obtaining an Fe(VI) salt such as $BaFeO_4$ by precipitation of another Fe(VI) salt such as K_2FeO_4. The synthetic method enables ferrates of $MFeO_4$ type to be obtained, where M represents either two alkali metal atoms, such as lithium, sodium, potassium or an alkaline earth metal atom, such as magnesium, calcium, barium. An alkali metal ferrate can be converted into an alkaline earth metal ferrate. The synthetic method of the invention also enables ferrates of $M(Fe,X)O_4$ type to be obtained, where M is defined as above and X is an atom selected from Al, Si, P, S, Cl, Mo, Mn and Cr. A method for the solid-state synthesis of an alkali metal sulphatoferrate or alkaline earth metal sulphatoferrate, of formula $M(Fe,S)O_4$, in which M represents two atoms of sodium/ potassium or one atom of calcium/ barium. This method makes use of the reaction of ferrous sulphate, $FeSO_4.7H_2O$ with calcium hypochlorite and potash. An improvement of this method is described where sodium hypochlorite is replaced by chlorine gas, Cl_2.

The iron(III) compound can be obtained from an iron(II) compound. An iron(II) compound notably a ferrous salt. A solution containing $FeSO_4$ in acid medium is used as iron source. This solution is neutralised by means of 30% soda at the rate of 150 ml per 100 ml of iron(II) solution. After neutralisation, the pH attains the value of 5.8, while the redox potential of the solution equilibrates around 168 mV/ECS. This value indicates that the iron is still in Fe(II) form. The solution is then oxidised by means of hydrogen peroxide, at the rate of 1.3 ml of 35% H_2O_2 per 50 ml of Fe(II) solution. The pH regulates during this oxidation to a value of 3.8. The end of the oxidation is indicated by the jump of potential which passes from 168 mV to +511 mV/ECS. This value indicates that the iron is in Fe(III) form. The filtrate only contains 39.2 mg/l of iron which thus indicates a high level of recovery of the iron.

The trivalent iron compound which can be used within the context of the invention is a ferric salt for example, notably ferric sulphate ($Fe_2(SO_4)_3$), which is hydrated or not, or an iron oxide, notably in the form of a pigment, such as goethite (α-FeOOH) or haematite (α-Fe_2O_3). The Fe(III) compound is advantageously in solid form. When this compound is in the form of a solution, the latter is advantageously neutralized in order to precipitate and recover the iron compound in solid form. The neutralization can be done for example with the aid of soda lime or magnesia.

The persulphate is indifferently used in sodium form ($Na_2S_2O_8$), potassium form ($K_2S_2O_8$) or ammonium form ($(NH_4)_2S_2O_8$). It is commercially available in sodium and potassium form. In general, the amount of persulphate is in a stoichiometric excess of about 1 to 15% with respect to the amount of iron (III) compound.

For the first time in 1702, Stahl noticed a red-purple colour during the explosive experiments which was created from a mixture of potassium nitrate and iron filings. The produced substance was eventually identified as hexavalent potassium ferrate (K_2FeO_4). Eckenberg and his colleague Becquerel observed the same colour in 1834 while heating a mixture of potassium hydroxide and iron ore. Later in 1840, Fremy formed the hypothesis that this colour was caused by a type of high-capacity iron with the chemical formula of FeO_3^{2-}. Despite these advances, the principles of hexavalent iron production began 100 years ago. (2)

FeO_4^{2-} and FeO_2^{4-} are powerful oxidizing agents used in advanced water treatment and organic synthesis. Preparation typically involves oxidizing iron(III) in strong alkaline conditions. In 1951, Thompson et al. described the preparation of potassium ferrate by the wet method. (3)

In this case, potassium ferrate was prepared according to the following scheme:

$$KMnO_4 + 8HCl \rightarrow MnCl_2 + 5/2Cl_2\uparrow + 4H_2O + KCl$$
$$Cl_2 + 2KOH \rightarrow KClO + KCl + H_2O$$
$$Fe(NO_3)_3{\cdot}9H_2O + 5KOH + 3/2KClO \rightarrow 3/2KCl + 23/2H_2O + K_2FeO_4 + 3KNO_3$$

This method of preparation gave a purity of only about 70% and a 10–15% yield. In the present study, an improved method of preparing solid phase potassium ferrate is proposed which gives a product of very high purity (99%) and a much greater yield (50–70%). Fe(VI) is relatively stable in an alkaline condition between pH 9–10. The characteristics of the solid potassium ferrate were analysed by X-ray diffraction (XRD) spectroscopy.

Ferrate preparation methods

The preparation methods of ferrate(VI) mainly include the dry oxidation method (4), the wet oxidation method (5) and the electrochemical method. (6) Among them, the electrochemical method has a simple operation process, simple preparation and high yield. (4)

1. Dry Oxidation (Solid-Phase Method Or Solid-Phase Melting Method)

This method involves iron filings or iron compounds with caustic alkali and peroxides (such as Na_2O_2) in a high-temperature environment. E. Martinez-Tamayo et al. (7) used Na_2O_2 and $FeSO_4$ to prepare sodium ferrate(VI) and then mixed it with a saturated potassium hydroxide solution and purified it to obtain solid potassium ferrate(VI). Talaiekhozani et al. (4) improved the reaction conditions. They found that, in the absence of O_2 and CO_2, Na_2O_2 reacts with iron oxide at a temperature of 370°C to form sodium ferrate(VI), as shown in Equation. The reaction under these conditions can reduce the possibility of explosion. L. Ninane et al. (8) reduced the cost of the preparation process to meet the needs in the actual water. Moreover, ferrous sulphate, potassium hydroxide and calcium hypochlorite (or chlorine) are used as raw materials and the reaction time is shortened.

The dry oxidation method can generate large quantities of high ferrate(VI), still, it is carried out under high temperature and high-pressure conditions and most of the reaction processes are exothermic, which increases the risk of explosion. The reaction also has high requirements for the alkaline corrosion resistance of the equipment, resulting in high preparation costs and difficulty in achieving industrial production. (9)

$$Fe_2O_3 + 3Na_2O_2 \xrightarrow{370^0C} 2Na_2FeO_4 + Na_2O$$

2. Wet Chemical Oxidation Method (Hypochlorite Method)

This is the most common laboratory method, relying on the oxidation of an iron(III) salt by a strong oxidizing agent (like sodium hypochlorite) in a highly concentrated basic solution. A ferric salt such as $Fe(NO_3)_3$ or $FeCl_3$ is mixed with a concentrated solution of sodium hydroxide and sodium hypochlorite. The solution turns a deep, characteristic purplish-black as ferrate(VI) forms. (10)

$$2FeCl_3 + 3NaOCl + 10NaOH \rightarrow 2Na_2FeO_4 + 9NaCl + 5H_2O$$

When added to aqueous systems, ferrate(VI) is a powerful oxidant that readily decomposes to ferric iron [$Fe(OH)_3$] and oxygen according to:

$2FeO_4^{2-} + 5H_2O \rightarrow 2Fe(OH)_3 + 3/2O_2 +$
$4OH^{-}$

Sodium Ferrate (Na_2FeO_4) is highly soluble in Potassium Hydroxide (KOH) is often added to the mixture. This causes the less soluble Potassium Ferrate (K_2FeO_4) to precipitate out of the solution. The precipitate is filtered and washed with organic solvents (like dry methanol) to remove excess alkali and impurities. (11)

$Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_3$
$2Fe(OH)_3 + 3NaClO + 4NaOH \rightarrow 2Na_2FeO_4 + 3NaCl +$
$5H_2O$
$Na_2FeO_4 + 2KOH \rightarrow K_2FeO_4 + 2NaOH$

Although the purity of ferrate(VI) prepared by the wet oxidation method reaches 96%, there are still problems of low yield and high preparation cost, so a green and efficient preparation method is needed.

3. Electrochemical Method

This process favoured due to its yield highly pure products. A pure iron or cast-iron anode is submerged in a highly concentrated alkaline electrolyte solution (e.g. NaOH or KOH). Under high anodic potentials a direct electrical current is applied, the iron anode oxidizes directly into ferrate(VI) ions and dissolves into the solution. The main reaction formula in the electrolysis process is shown in Equations. (12-13)

Anode reactions: $Fe + 8OH^{-} \rightarrow FeO_4^{-2} + 4H_2O + 6e^{-}$

Cathode reaction: $2H_2O + 2e- \rightarrow H_2 + 2OH^{-}$

General reaction: $Fe + 2OH^{-} + 2H_2O \rightarrow FeO_4^{-2} + 3H_2$

$FeO_4^{2-} + 2K^{+} \rightarrow K_2FeO_4$

Ferrates are unstable in aqueous or acidic solutions and decompose rapidly, releasing elemental oxygen. To remains stable ferrate must be kept dry or in highly alkaline conditions. Due to ferrate shows strong oxidizing capabilities, ferrates are highly effective for water purification, as they can simultaneously disinfect water and degrade heavy metals or complex organic pollutants.

Another example is the production of $BaFeO_4$ directly by the electrochemical method. This method uses the oxidation of an iron wire as the anode electrode in a common electrolyte of NaOH / $Ba(OH)_2$. Throughout the electrolysis, the concentration of $BaFeO_4$ increases. (14) The produced $BaFeO_4$ can be filtered to separate it from electrolyte and then it must be rinsed three times with distilled water.

III. PROCEDURE OF PREPARATION OF FERRATE

One liter of KOH concentrated solution is prepared with Barnstead model D4742 deionized water from 0.620 kg of KOH pellets from Fruitarom, Haifa, Israel (Analytical reagent KOH). The solution is converted to potassium hypochlorite by reaction with chlorine. The Cl_2 is generated in-house within a 2 liter Woulff (spherical) flask with fritted glass connections. The glass connections are attached to a 1 liter dropping flask with pressure equalizer inlet (with a burette controlled liquid inlet and another connection is to a gas-outlet). In the Woulff flask is 0.25 kg $KMn0_4$ (99% CP grade, Fruitarom), and from the dropping flask 1.13 liter of 37% HC1 (AR grade, Carlo-Erba) is added drop-wise to the $KMn0_4$ to generate chlorine in accord with:

$KMn0_4 + 8HC1 \rightarrow MnCl_2.4H_20 + KC1 + 5/2Cl_2$

Droplets, HC1 and water are removed from the evolved Cl_2, through a series of 2 liter Dreschel (gas washing) flasks connected in series. The first and third are empty (to prevent backflow); the second contains water (to remove HC1), the fourth contains 95-98% H_2S0_4 (to remove water), and the fifth flask contains glass wool (to remove droplets). The evolved, cleaned Cl_2 flows into a reaction chamber (a sixth Dreschel flask containing the concentrated KOH solution and surrounded by an external ice-salt bath) where it is stirred into concentrated KOH solution. Excess gas is trapped within a final flask containing waste hydroxide solution. Chlorination of the KOH solution generates hypochlorite, which is continued until the weight of the concentrated KOH solution has increased by 0.25 kg, over a period of approximately 90 minutes, in accord with:

$2KOH + Cl_2 \rightarrow KCIO + KC1 + H_20$

This hypochlorite solution is cooled to 10°C. Alkalinity of the solution is increased and KC1 removed, through the addition of 1.46 kg KOH pellets, added slowly with stirring, to permit the solution temperature to rise to not more than 30°C. Stirring is continued for 15 minutes, and the solution is cooled to 20°C. The precipitated KC1 is removed by filtration through a 230 mm diameter porcelain funnel using a glass microfibre filter.

A ferric salt is added to the hypochlorite solution, reacting to Fe(VI), as a deep purple $Fe0_4^{-2}$ solution. An external ice-salt bath surrounds the solution to prevent overheating. Specifically, to the alkaline potassium hypochlorite solution at 10°C, is added 0.315 kg ground $Fe(N0_3)_3.9H20$ (98% ACS grade, ACROS). In alkaline solution, the ferric nitrate constitutes hydrated ferric oxides or hydroxides, summarized as:

$Fe(N0_3)_3.9H_20 + 30H^{-} \rightarrow Fe(OH)_3 + 9H_20 + 3N0_3^{-}$

which is oxidized by hypochlorite to form the Fe(VI) anion, $Fe0_4^{2-}$ in solution:

$Fe(OH)_3 + 3/2C10^- + 20H^- \rightarrow Fe0_4^{2-} + 3/2C1^- + 5/2H_20$

During the ferric addition, a surrounding ice-salt bath is applied to maintain the solution temperature below 35°C. Following this addition, the solution is stirred for 60 minutes, with the solution temperature controlled at 20°C. For potassium salts, the overall reaction is summarized by above equations.

$Fe(N0_3)_3.9H_20 + 3/2KC10 + 5K0H \rightarrow K_2Fe0_4 + 3/2KCl + 3KN0_3 + 23/2H_20$

Following this, the KOH concentration of the resultant Fe(VI) solution is increased to precipitate K_2Fe0_4. Specifically, into this solution is stirred 1.25 liter of 0°C, 9.6 M KOH. After 5 minutes, the suspension is (simultaneously) filtered onto two 120 mm P-l sintered Duran glass filters (Schott). The two precipitates are dissolved in 1.6 liter of 2.57 M KOH, and quickly filtered, through a funnel with 2 layers of GF/A filter paper of 230 mm diameter, directly into 1.7 liter of 0°C 12 M KOH. The solution is stirred for 15 minutes at 3°C, and then the solution is filtered onto a 90 mm P-2 sintered Duran glass filter (Schott). The wet K_2Fe0_4 is dissolved in 0.850 liter of 0°C 2.57 M KOH solution, and quickly filtered on 2 sheets of filter paper GF/A 150 mm diameter, in a filtering flask which contains 2.7 liters of a 12 M KOH solution. From this point, two grades of K_2Fe0_4 are produced. The first generates higher yield, 90 g K_2Fe0_4, at a purity of 96-97%. The second generates 80 g of K_2 $Fe0_4$ at even higher purity 97-98.5%. In both procedures, the wet K_2Fe0_4 is redissolved in 0.850 liter of 0°C 2.57 M KOH solution, and quickly filtered on 2 sheets of filter paper GF/A 150 mm diameter, into a filtering flask containing 2.7 liter 12 M KOH solution. The resulting suspension is stirred for 15 minutes at 0°C and is filtered through a P-2 sintered glass filter. This redissolution /filtering step is repeated in the second (highest purity) procedure. In either procedure, on the same filter, the precipitate is successively rinsed: 4 times with 0.16 liter n-hexane; 2 times with 0.08 liter isopropyl alcohol; 8 times with 0.15 liter methanol and finally 3 times with 0.080 liter diethyl ether. The K_2Fe0_4 is dried for 30-60 minutes under room temperature vacuum (at 2-3 mbar).

IV. VARIOUS TYPES OF FERRATES

Sodium ferrate Na_2FeO_4 solution was prepared by taking required quantity of ferric nitrate [$Fe(NO_3)_3.9H_2O$] in a 50 ml beaker and then required amount of sodium hypochlorite solution was added drop-wise with constant stirring.

Formation of clear dark purple red coloured solution indicated the formation of ferrate di-anions in the solution. (15-18) Similar to the case of oxidation of ferric chloride by sodium hypochlorite, the oxidation of ferric nitrate may be shown by equation.

$2Fe(NO_3)_3 + 3NaClO + 10NaOH \rightarrow 2Na_2FeO_4 + 6NaNO_3 + 3NaCl + 5H_2O$

The Cs_2Fe0_4 and $Rb(K)Fe0_4$ salts were synthesized from potassium ferrate, by driving formation via their hydroxide reaction, in the respective cesium or rubidium hydroxide solution. In these media, effective Fe(VI) cesium or rubidium salts are observed in the precipitation reaction:

$K_2Fe0_4(aq) + 2MOH(aq) \rightarrow M_2Fe0_4(s) + 2KOH(aq)$ (M=Cs or Rb)

Or in the case of partial replacement:

$K_2Fe0_4(aq) + xMOH(aq) \rightarrow M_xK_{(2-x)}Fe0_4(s) + xKOH(aq)$

A solution of 1.7g K_2Fe0_4 in 7ml 0.5% aqueous KOH, 4.4g of $CsOH.xH_20$ (from Aldrich) dissolved in 1.4 ml deionized water, at 0°C, was added, while maintaining 0°C using an ice bath. After 5 minutes of vigorous stirring and filtration on a sintered glass funnel the precipitate was washed sequentially with the following organic solvents: n-hexane (4 times washings, each with 5ml), iso-propanol (2 times washings, each with 5ml), methanol (8 times washings, each with 5ml) and finally with diethyl ether (3 times washings, each with 5ml). The resultant Cs_2Fe0_4 was dried for 2 hours under room temperature vacuum (at 2-3 mbar) yielding 2.4 g Cs_2Fe0_4.

As the synthesis of alkali metal Fe(VI) salts, the dried, solid state stable K_2Fe0_4 may be used for alkaline earth metal Fe(VI) salts, $BaFe0_4$ and $SrFe0_4$ synthesis, directly or after storage. The salts were synthesized by utilizing the higher alkaline insolubility of strontium or barium ferrate(VI) compared to that of potassium ferrate(VI). (19, 20) We have observed effective Fe(VI) precipitates occur starting with barium nitrate, chloride, acetate or hydroxide salts. $SrFe0_4$ and $BaFe0_4$ may also be prepared from the respective acetate salts in accordance with the reaction:

$K_2Fe0_4(aq) + M(C_2H_30_2)_2(aq) \rightarrow MFe0_4(s) + 2KC_2H_30_2(aq)$ (M=Sr or Ba)

A 1:1 mole ratio of $Ba(OH)_2.8H_20$ to K_2Fe0_4 yields upon grinding an immediate reaction to $BaFe0_4$.

$K_2Fe0_4 + Ba(OH)_2.8H_20 \rightarrow BaFe0_4 + 2KOH + 8H_20$

Upon dissolving the potassium ferrate salt in an aqueous solution of silver nitrate, a spontaneous, immediate black precipitate of silver ferrate was obtained:

$K_2Fe0_4 + 2AgN0_3 \rightarrow Ag_2Fe0_4 + 2KN0_3$

V. FERRATE (VI) MEASUREMENT METHODS

Researchers have mentioned two methods for measuring ferrate(VI) in aquatic environments which includes the titration and spectrophotometry methods. (21) One of the most appropriate methods in measuring ferrate(VI) is its reaction with chromite salt. The following reaction explains the reaction between ferrate(VI) and chromite in an acidic environment. (22) In this method, sodium diphenylamine-4-sulfonate is used as an indicator. It should be noted that this method can only be applied for solutions with low ferrate(VI) ion concentrations.

$Cr(OH)_4^- + FeO_4^{2-} + 3H_2O \rightarrow Fe(OH)_3(H_2O)_3 + CrO_4^{2-} + OH^-$

Another way to measure ferrate(VI) is to convert it into Fe(III) in an alkaline environment along with arsenite. (23) In this method, a weighed quantity of ferrate(VI) iron salt is added to a solution containing arsenite, in which the concentration must be higher than the required amount for the conversion of ferrate(VI) to Fe(III). (24) The remaining arsenite can then be measured by the bromate and cerate standard solutions. By measuring the concentration of bromate and cerate, the ferrate(VI) ion can then be measured.

$2FeO_4^{2-} + 3AsO_3^{3-} + 11H_2O \rightarrow 2Fe(OH)_3(H_2O)_3 + 3AsO_4^{3-} + 4OH^-$

$2BrO_3^- + 5AsO_3^{3-} + 2H^+ \rightarrow Br_2 + 5AsO_4^{3-} + H_2O$

$2Ce^{4+} + AsO_3^{3-} + H_2O \rightarrow 2Ce^{3+} + AsO_4^{3-} + 2H^+$

Ferrate concentration was measured with an indirect spectrophotometric method using an ABTS (2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)) reagent (Sigma-Aldrich). In the presence of excess ABTS, ferrate(VI) oxidizes. ABTS with a 1:1 M ratio, producing a light-absorbing radical cation ($ABTS^{\bullet+}$) with a visible UV-absorption maxima at 415 nm. (25-27)

Ferrate standards and samples were analyzed using a UV–vis spectrophotometer and a 1 cm quartz cuvette. Ferrate standards were prepared using potassium ferrate (99%) in a concentration range of 0–10 mM. Ferrate(VI) was also directly analyzed using direct UV–vis spectrophotometry at 530 nm in 1 and 5 cm quartz cuvettes, in a concentration range of 0–2 mM with co-occurring Fe^{3+} (dosed with $FeCl_3$), to simulate water matrix conditions during electrolysis experiments and to understand the effects on UV-absorbance and ferrate(VI) stability. Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) were also pursued for a limited number of tests.

Free chlorine concentrations were also monitored using the DPD (*N*,*N*-diethyl-*p*-phenylenediamine) reagent and a DR 300 colorimeter.

The Scanning electron microscopy (SEM) is used to characterise the ferrate(VI) salts in the powder form by providing some micrographs or structural images of the product. The XRD (X-Ray powder Diffraction method) is another method which goes together with FT-IR and SEM analysis in order to confirm the crystallinity, structures and magnetic properties of the ferrate(VI) salts. The XRD is one of the analytical facilities used to indicate the presence of ferrate(VI) by demonstrating the isomorphism with other ferrate salts obtained in the literature. (28-29) Mössbauer spectroscopy allows detecting the oxidation state of iron. It can help to determine the degradation rate of Fe(VI) in ferrate(VI) ion over time. It also helps to check the presence of a magnetic order at low temperature. (28, 30)

Direct colorimetry can also be used to identify ferrate(VI) in solution, (25, 31) at a much lower molar absorption coefficient than that of ABTS; therefore, higher concentrations and/or longer UV path lengths are required. Using a 5 cm quartz cuvette, both the BDD and NAT electrogenerated ferrates were analysed. The UV absorbance spectra confirmed the qualitative observations, whereby the solution produced with the NAT electrode showed evidence of ferrate(VI) with an absorbance maximum at 526 nm. (32) This peak is slightly higher than that of ferrate(VI) observed with the chemical standard (using K_2FeO_4) and the peak shapes are notably different with a maximum at 524 nm.

Oxidant probe species and micropollutants, namely nitrobenzene (NB), carbamazepine (CBZ) and fluconazole (FCZ) (Sigma-Aldrich) were quantified using high performance liquid chromatography (HPLC) equipped with a ZORBAX Eclipse XDB-C18 column and a UV detector at 254, 285 and 205 nm, respectively. The mobile phase, flowing at 0.5 mL min^{-1}, was a composition of water with 0.1% formic acid and acetonitrile (ACN) under the gradient: 0 min, 10% ACN; 2 min, 10% ACN; 6 min, 95% ACN; 8 min, 95% ACN; 9 min, 10% ACN; 12 min, 10% ACN. An injection volume of 20 µL was used with a total runtime of 12 min for each sample.

VI. CHEMICAL STRUCTURE OF HEXAVALENT IRON

The X-ray spectroscopy studies on a solid crystal like K_2FeO_4 suggested that ferrate(VI) is shaped from four oxygen atoms which establish a covalent bond with a central iron atom with an oxidation number of +6. (32-33) The tetrahedral structure of ferrate(VI) is confirmed through oxygen isotopic studies in an aqueous solvent and suggests that four oxygen atoms surround the iron atom. (34)

Other researches have demonstrated that ferrate(VI) ion can have three resonance hybrid structures with the atoms of oxygen.

VII. STABILITY OF FERRATE(VI)

Stability of ferrate(VI) solution depends on factors such as coexisting ions in the solution, temperature, pH and concentration of the solution. The stability of ferrate(VI) is one of the problems limiting its large-scale preparation and application. Because ferrate(VI) is poorly stable and difficult to store, most of the current applied research on ferrate(VI) is limited to the laboratory. The storage environment requirements for ferrate(VI) are more stringent and require low temperature and dry storage. Once removed from the dry environment, ferrate(VI) is highly susceptible to the influence of water molecules. Its stability will rapidly decrease and oxidative decomposition will occur, with the following reaction Equation.

$$4FeO_4^{-2} + 10H_2O \rightarrow 4Fe(OH)_3 + 3O_2\uparrow + 8OH^-$$

The main factors affecting the stability of ferrate(VI) include the temperature of the solution, pH and the coexistence of ions in the solution. The temperature has an important influence on the stability of ferrate(VI); the higher the temperature, the faster the decomposition rate of ferrate(VI) (35), so it is necessary to maintain a relatively low temperature in the process of electrolysis and oxidation preparation of ferrate(VI). Ferrate(VI) exists in four main forms, including $H_3FeO_4^+$, H_2FeO_4, $HFeO_4^-$ and FeO_4^{2-}. Under acidic conditions, $H_3FeO_4^+$ and H_2FeO_4 are the main forms, while $HFeO_4^-$ and FeO_4^{2-} are the main forms under neutral or alkaline conditions. FeO_4^{2-} is extremely unstable and easy to decompose under an acidic environment, while FeO_4^{2-} has strong stability when pH is controlled at 9~10. The main reaction equations for FeO_4^{2-} under acid–base conditions are shown in Equations given below.

$$\text{Acidic: } FeO_4^{-2} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O$$

$$\text{Alkaline: } FeO_4^{-2} + 4H_2O + 3e^- \rightarrow Fe(OH)_3 + 5OH^-$$

In addition to the above influencing factors, the components in the ferrate(VI) solution can also affect the rate of its decomposition. When the ferrate(VI) solution contains phosphate, it can hinder the decomposition rate of the ferrate(VI). At the same time, light also has a particular influence on the stability of ferrate(VI) (36); ultraviolet light irradiation will accelerate the decomposition rate of ferrate(VI), so attention should be paid to avoiding light during storage.

VIII. BACKGROUND

Ferrate refers to a hexavalent iron compound and is the only stable high-valence iron compound. Ferrate has strong oxidizing property and the final product of the reaction with organic matters is non-toxic and harmless ferric ions, so ferrate can be used as a multifunctional green water treatment chemical agent integrating oxidation, flocculation and sterilization; moreover, the super-iron battery using ferrate as a cathode material has great attraction due to the characteristics of large capacity, good charging property, strong conductivity, environmental friendliness and in organic synthesis, ferrate has the characteristic of selective oxidation, thereby providing an effective way for the clean production of organic synthesis; ferrate is used as a matrix, transient particles Fe(IV) and Fe (V) can be generated by a pulse radiolysis technology and the two strong oxidizing particles are researched to fill the blank in the field. The existing ferrate preparation process has the disadvantages of low yield, high preparation cost and the industrial production is not yet mature, which limits the practical application thereof.

IX. APPLICATION

Fe(VI) in the form of potassium ferrate (K_2FeO_4) has been found to be a powerful oxidant over a wide pH range and many studies have considered its role as an oxidant in water and wastewater treatment (Jiang and Lloyd, 2002). Ferrate(VI) has been applied for removal of pollutants such as medicines, ammonium, cyanides, sulphides, phosphates, arsenic, estrogens, anilines and phenols. (37-38)

Ferrate(VI) is a hexavalent iron salt with strong oxidation and redox potential up to 2.20 V under acidic conditions and its oxidation performance is higher than other common strong oxidants (such as ozone, chlorine and potassium permanganate). The redox product of ferrate(VI) is a non-toxic and harmless ferric iron salt that can be used as a flocculant to improve the removal of pollutants (39), and does not produce toxic by-products compared to chlorine and ozone treatment (40), so it also has good potential for use in pollutant degradation and removal. Ferrate(VI) is often used as an oxidizing agent to remove pharmaceuticals and personal care products, phenolic compounds and algae.

X. CONCLUSION

The reduction product Fe(III) or iron hydroxide of ferrate(VI) has a strong coagulating effect that can adsorb particles in water and reduce turbidity. Therefore, the reduced product of ferrate(VI) can also be used as a coagulant.

Ferrate(VI) is a highly efficient water treatment agent that combines the functions of oxidation, disinfection, adsorption and flocculation. Ferrate(VI) has strong oxidizing properties and is effective at pollutant removal. Ferrate(VI) is very widely used in the field of water treatment. Due to its strong oxidizing properties, it can remove most organic pollutants and algae from the water. The disadvantage of ferrate(VI) is that it is unstable. Oxidization of pollutants using ferrate(VI) does not produce any toxic and mutagenic byproducts, it is known as a green technology and ferrate(VI) is known as green chemical.

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