Optimization of Five Reducing Agents using UV-VIS Spectrometry for Reduction of Iron(III) to Iron(II)

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This study aims to investigate the optimum conditions of five reducing agents viz., sodium thiosulfate (Na₂S₂O₃), hydroxylamine hydrochloride (NH₂OH·HCl), ascorbic acid (C₆H₈O₆), sodium oxalate (Na₂C₂O₄) and sodium sulfite (Na₂SO₃) for the reduction of Fe(III) to Fe(II) using UV-Vis spectrometry. As result, the optimum pH of acetate buffer for Na₂S₂O₃, NH₂OH·HCl, C₆H₈O₆, Na₂C₂O₄ and Na₂SO₃ were obtained at pH 4.5, 4.5, 4.5, 5.0 and 4.0, respectively. Whilst the optimum time for each Na₂S₂O₃, NH₂OH·HCl and C₆H₈O₆ were 15 min, the outcome for Na₂C₂O₄ and Na₂SO₃ took longer time which are 45 and 30 min, respectively. As for optimum concentration, the results were various as Na₂S₂O₃, NH₂OH·HCl, C₆H₈O₆, Na₂C₂O₄ and Na₂SO₃ were at 11, 7, 5, 12 and 60 ppm in consecutive order. Also to conclude the work, the recovery percentage were calculated and the results were Na₂S₂O₃ (102.81 %), NH₂OH·HCl (116.71 %), C₆H₈O₆ (97.97 %), Na₂C₂O₄ (85.89 %), and Na₂SO₃ (85.04 %).

Keywords: Iron, 1,10-Phenanthroline, Reducing Agents, UV-vis spectrometry.

INTRODUCTION

The widespread use of iron has caused to increase environmental pollution, including in the ground water. The two main sources of groundwater contamination are the leakage of organic chemicals from chemical storage in underground bunker and industrial waste storage space contained by ponds or near water sources [1]. Some methods of iron analysis have been done in previous studies including atomic absorption spectrometry (AAS) [2], chromatography [3], inductively coupled plasma-mass spectrometry (ICP-MS) [4], inductively coupled plasma-optical emission spectrometry (ICP-OES) [5], sensors [6], anodic or cathodic stripping and voltammetry [7] and UV-Vis spectrometry [8]. The colorimetry method is quite affordable but their disadvantage is less sensitive than using UV-Vis spectrometry. UV-visible spectrometry has the advantage of measuring the iron in the form of ions, both Fe³⁺ and Fe²⁺. The solution was analyzed using UV-visible spectrometry, thus iron complex must be generated as coloured complex [9]. Different types of complexing agents are commonly used, such as thiocyanate acid, molybdenum, 1,10-phenanthroline, thioglycolic acid and ferrozine. However, 1,10-phenanthroline is most widely used to determine Fe³⁺ and Fe²⁺ because it is selective, direct and does not need sample extraction [10].

In this study, UV-visible spectrometry was used to determine the iron content. It started by reducing Fe³⁺ to Fe²⁺ with the addition of reducing agent. Amelia [11] examined the reducing ability of Na₂S₂O₃ and obtaining Fe²⁺ % recovery at 99.2243 %. Further studies were conducted to reduce Na₂S₂O₃ and K₂C₂O₄, obtained % recovery for Na₂S₂O₃ was 77.93 % and for K₂C₂O₄ was 72.77 % [12]. In this study, we analyzed the optimum conditions to reduce Fe³⁺ to Fe²⁺ by comparing five reducing agents are Na₂S₂O₃, NH₂OH·HCl, C₆H₈O₆, Na₂C₂O₄ and Na₂SO₃.

EXPERIMENTAL

The chemicals iron(III) chloride hexahydrate, 1,10-phenanthroline and sodium acetate procured from Merck. Sodium thiosulfate pentahydrate, hydroxylamine hydrochloride, ascorbic acid, sodium oxalate, 99 % sodium sulphite and 99 % acetone are obtained from SPAM Chemical.
Standard solution: The standard solution of Fe$^{3+}$ was prepared by dissolving 0.0484 g FeCl$_3$·6H$_2$O in a beaker containing a small amount of deionized water. The formed solution was then poured into a 100 mL measuring flask and diluted.

Reducing agents solution: For reducing agent Na$_2$S$_2$O$_3$ solution is made by dissolving 0.0157 g Na$_2$S$_2$O$_3$·5H$_2$O in a beaker containing a small amount of deionized water. The formed solution was then poured into a 100 mL measuring flask and diluted.

The reducing agent NH$_2$OH·HCl solution was prepared by dissolving 0.01 g NH$_2$OH·HCl in a beaker containing a small amount of deionized water. The formed solution was then poured into a 100 mL measuring flask and diluted.

1,10-Phenanthroline solution was prepared by dissolving 1.10 g C$_{12}$H$_8$O$_2$ in a beaker with a small amount of deionized water. The formed solution was then put into a 100 mL measuring flask and diluted. The solid Na$_2$C$_2$O$_4$, Na$_2$S$_2$O$_3$, or Na$_2$SO$_3$ solution of 100 ppm was pipetted 1.1 mL and added into a 10 mL measuring flask with 1.5 mL 1,10-phenanthroline 1000 ppm, 1.5 mL buffer acetate pH 4.5 and 5 mL of acetone. Then, the solution was diluted with deionized water.

Acetate buffer solution: Buffer acetate solution pH 4.5 was prepared by dissolving 1.31 g of sodium acetate in deionized water until dissolved. The acetate buffer solution pH 4.5 was fed into 100 mL measuring flask and then 5 mL acetic acid diluted with deionized water. Furthermore, acetate buffer solution varied in pH (3.0; 3.5; 4.0; 4.5; 5.0).

Blank solution: The reducing agent NH$_2$OH·HCl, Na$_2$S$_2$O$_3$, C$_6$H$_8$O$_2$, Na$_2$C$_2$O$_4$, or Na$_2$SO$_3$ solution of 100 ppm was pipetted 1.1 mL and added into a 10 mL measuring flask with 1.5 mL 1,10-phenanthroline 1000 ppm, 1.5 mL buffer acetate pH 4.5 and 5 mL of acetone. Then, the solution was diluted with deionized water.

Wavelength determination: A standard solution of 100 ppm Fe(III) (0.5 mL) was added into a 10 mL measuring flask, then added a reducing agent solution. Later, the mixture was added with 5 mL of acetone and diluted with deionized water. After that the solution was shaken and left for 15 min and measured using UV-VIS.

Determination of pH optimum: The treatment was almost the same as wavelength determination, only done by varying the pHs (3.0; 3.5; 4.0; 4.5; 5.0; 5.5; 6.0). Then the mixture, 1.5 mL of 1,10-phenanthroline (1000 ppm) and 5 mL of acetone, then diluted with deionized water. After that the solution was shaken and left for 15 min and measured its absorbance.

Determination of optimum time: A standard solution of 100 ppm Fe(III) (0.5 mL) was added into a reducing agent solution. The mixture was added with 1.5 mL acetate buffer at optimum pH. Afterward, the mixture was added with 1.5 mL 1,10-Phenantrinol 1000 ppm and 5 mL of acetone then diluted with deionized water. The variation time for complex formation was measured at 0, 15, 30, 45, 60 min.

**Results and discussion**

Determination of the maximum wavelength of Fe(II)-1,10-phenanthroline can be seen from the highest absorbance value from the UV-vis spectrometry. In this study, FeCl$_3$·6H$_2$O was used. First, Fe$^{3+}$ solution was reduced to Fe$^{2+}$ with five reducing agents, namely: sodium thiosulfate, hydroxylamine hydrochloride, ascorbic acid, sodium oxalate and sodium sulfite which were mixed with 1,10-phenanthroline solution at different pHs (4.0; 4.5 and 5.0) with a connection between 15-45 min, then measured with a UV-visible spectrometry. The reaction of Fe(II) with reducing agents can be shown eqns. 1-5:

\[
\begin{align*}
2\text{Fe}^{3+}(aq) + 2\text{S}_2\text{O}_3^{2-}(aq) & \rightarrow 2\text{Fe}^{2+}(aq) + \text{S}_4\text{O}_6^{2-}(aq) \quad (1) \\
4\text{Fe}^{3+}(aq) + 2\text{NH}_2\text{OH}·\text{HCl}(aq) & \rightarrow 4\text{Fe}^{2+}(aq) + \text{N}_2\text{O}(aq) + 4\text{H}^+(aq) + \text{H}_2\text{O}(l) \quad (2) \\
2\text{Fe}^{3+}(aq) + \text{C}_6\text{H}_5\text{O}_6^{2-}(aq) + 2\text{H}_2\text{O}(l) & \rightarrow 2\text{Fe}^{2+}(aq) + \text{C}_6\text{H}_5\text{O}_6^{2-}(aq) + 2\text{H}_2\text{O}(l) \quad (3) \\
2\text{Fe}^{3+}(aq) + \text{C}_2\text{O}_4^{2-}(aq) & \rightarrow 2\text{Fe}^{2+}(aq) + 2\text{CO}_2(aq) \quad (4) \\
2\text{Fe}^{3+}(aq) + \text{SO}_4^{2-}(aq) + \text{H}_2\text{O}(l) & \rightarrow 2\text{Fe}^{2+}(aq) + \text{SO}_4^{2-}(aq) + 2\text{H}^+(aq) \quad (5)
\end{align*}
\]

The resulting wavelength is found to be 510 nm for five reducing agents (Fig. 1). The colour of complex Fe(II)-1,10-phenanthroline solution is red orange, stable under acidic or alkaline conditions that are in the range of pH 2-9, but for this study, it is carried out in an acidic media using an acetate buffer solution. Alkaline buffers are not selected because OH$^-$ ions are ligands that often compete with 1,10-phenanthroline ligands. To determine the effect of pH on the absorption of Fe(II). The results of optimum pH is shown in Table-2.
The reduction time is the formation of Fe(II)-1,10-phenanthroline complexes. All Fe^{2+} ions can bind 1,10-phenanthroline ligand and form complexes. To improve the performance of Fe(II)-1,10-phenanthroline, it is necessary to produce optimal time. A time variation was used to influence the time of reduction from 0 to 60 min. The optimum time of determination of Fe(II)-1,10-phenanthroline complex formation with each reducing agent was carried out at optimum pH, respectively. The results of time optimum are shown in Table-3.

<table>
<thead>
<tr>
<th>Reducing agent</th>
<th>Time (min)</th>
<th>Absorbance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na_{2}S_{2}O_{3}</td>
<td>15</td>
<td>0.320</td>
</tr>
<tr>
<td>NH_{2}OH·HCl</td>
<td>15</td>
<td>0.799</td>
</tr>
<tr>
<td>C_{6}H_{8}O_{6}</td>
<td>15</td>
<td>0.610</td>
</tr>
<tr>
<td>Na_{2}C_{2}O_{4}</td>
<td>45</td>
<td>0.268</td>
</tr>
<tr>
<td>Na_{2}SO_{3}</td>
<td>30</td>
<td>0.406</td>
</tr>
</tbody>
</table>

Determination of optimum concentration the reducing agent aims to decide at what concentration to be for reduce Fe^{3+} ion to Fe^{2+} ion with complexing 1,10-phenanthroline at an acidic atmosphere. The results of concentration optimum are shown in Table-4. Based on Fig. 2a, the peak of optimum concentration reducing agents NH_{2}OH·HCl is 11 ppm and C_{6}H_{8}O_{6} is 7 ppm. But the peak was out of Lambert-Beer range.
(0.2-0.8). So, to comply with the regulation, the concentration of NH$_2$OH-HCl was adjusted to 8 ppm with absorbance 0.693 and C$_6$H$_8$O$_6$ was adjusted to 5 ppm with absorbance 0.762.

In this work, the value of percentage recovery was obtained from five reducing agents at optimum conditions (pH, time, and concentration). In this study, it can be stated that this data is good and can be used for further measurement because it is in the range of 80-100 % with accuracy level is 95 % (Table-5).

### TABLE-4

<table>
<thead>
<tr>
<th>Reducing agent</th>
<th>Concentration (ppm)</th>
<th>Absorbance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$S$_2$O$_3$</td>
<td>11</td>
<td>0.455</td>
</tr>
<tr>
<td>NH$_2$OH-HCl</td>
<td>8</td>
<td>0.693</td>
</tr>
<tr>
<td>C$_6$H$_8$O$_6$</td>
<td>5</td>
<td>0.762</td>
</tr>
<tr>
<td>Na$_2$C$_2$O$_4$</td>
<td>12</td>
<td>0.209</td>
</tr>
<tr>
<td>Na$_2$SO$_3$</td>
<td>60</td>
<td>0.389</td>
</tr>
</tbody>
</table>

### TABLE-5

<table>
<thead>
<tr>
<th>Reductors</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$S$_2$O$_3$</td>
<td>103.440</td>
</tr>
<tr>
<td>NH$_2$OH-HCl</td>
<td>116.007</td>
</tr>
<tr>
<td>C$_6$H$_8$O$_6$</td>
<td>98.068</td>
</tr>
<tr>
<td>Na$_2$C$_2$O$_4$</td>
<td>85.886</td>
</tr>
<tr>
<td>Na$_2$SO$_3$</td>
<td>84.590</td>
</tr>
</tbody>
</table>

**Conclusion**

Based on the results of this study, it is concluded that the best reducing agent for reducing iron(III) to iron (II) using UV-visible spectrometry with maximum wavelength 510 nm is hydroxylamine hydrochloride (NH$_2$OH-HCl) with optimum pH at pH 4.5, optimum time for 15 min at a concentration of 8 ppm. The second best reducing agent is ascorbic acid (C$_6$H$_8$O$_6$) with optimum pH at pH 4.5, optimum time for 15 min at a concentration of 5 ppm. The recovery percentage for different reducing agents were found to be as 87.68 % (for Na$_2$S$_2$O$_3$), 116.00 % (for NH$_2$OH-HCl), 98.068 % (for C$_6$H$_8$O$_6$), 85.97 % (for Na$_2$C$_2$O$_4$) and 103.44 % (for Na$_2$SO$_3$).

**CONFLICT OF INTEREST**

The authors declare that there is no conflict of interests regarding the publication of this article.

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