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 ($Na_2S_2O_3$), hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), ascorbic acid ($C_6H_8O_6$), sodium oxalate ($Na_2C_2O_4$) and sodium sulfite (Na_2SO_3) for the reduction of Fe(III) to Fe(II) using UV-Vis spectrometry. As result, the optimum pH of acetate buffer for $Na_2S_2O_3$, $NH_2OH \cdot HCl$, $C_6H_8O_6$, $Na_2C_2O_4$ and Na_2SO_3 were obtained at pH 4.5, 4.5, 4.5, 5.0 and 4.0, respectively. Whilst the optimum time for each $Na_2S_2O_3$, $NH_2OH \cdot HCl$ and $C_6H_8O_6$ were 15 min, the outcome for $Na_2C_2O_4$ and Na_2SO_3 took longer time which are 45 and 30 min, respectively. As for optimum concentration, the results were various as $Na_2S_2O_3$, $NH_2OH \cdot HCl$, $C_6H_8O_6$, $Na_2C_2O_4$ and Na_2SO_3 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 $Na_2S_2O_3$ (102.81 %), $NH_2OH \cdot HCl$ (116.71 %), $C_6H_8O_6$ (97.97 %), $Na_2C_2O_4$ (85.89 %), and Na_2SO_3 (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 Fe^{3+} and Fe^{2+}. 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 Fe^{3+} and Fe^{2+} 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 Fe^{3+} to Fe^{2+} with the addition of reducing agent. Amelia [11] examined the reducing ability of $Na_2S_2O_3$ and obtaining Fe^{2+} % recovery at 99.2243 %. Further studies were conducted to reduce $Na_2S_2O_3$ and $K_2C_2O_4$, obtained % recovery for $Na_2S_2O_3$ was 77.93 % and for $K_2C_2O_4$ was 72.77 % [12]. In this study, we analyzed the optimum conditions to reduce Fe^{3+} to Fe^{2+} by comparing five reducing agents are $Na_2S_2O_3$, $NH_2OH \cdot HCl$, $C_6H_8O_6$, $Na_2C_2O_4$ and Na_2SO_3.

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 $FeCl_3 \cdot 6H_2O$ 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 $Na_2S_2O_3$ solution is made by dissolving 0.0157 g $Na_2S_2O_3 \cdot 5H_2O$ 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 $NH_2OH \cdot HCl$ solution was prepared by dissolving 0.01 g $NH_2OH \cdot HCl$ in a beaker containing a small amount of deionized water. The formed solution was then poured into a 100 mL measuring flask and diluted.

Ascorbic acid $(C_6H_8O_6)$ solution was made by dissolving 0.01 g of $C_6H_8O_6$ 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 $Na_2C_2O_4$ weighed to 0.05 g, put into a 100 mL beaker and 50 mL deionized water added. The mixture was heated over hot plate at 60 ºC while stirring until the solid is completely dissolved. After that sodium oxalate solution was kept to cool and transferred into a 100 mL measuring flask. Finally, deionized water was added and dilute the solution to the measured mark and was shaken until becomes homogeneous solution.

For preparing the solution of Na_2SO_3, it was made by dissolving 0.1 g Na_2SO_3 in a beaker containing a small amount of deionized water. The formed solution was further diluted to 100 mL.

1,10-Phenanthroline solution was prepared by dissolving 0.1 g of 1.10-phenanthroline into 100 mL beaker containing 50 mL deionized water. The mixture was heated to 60 ºC with stirring. Then the solution was allowed to cool and put into a 100 mL measuring flask and 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 $NH_2OH \cdot HCl$, $Na_2S_2O_3$, $C_6H_8O_6$, $Na_2C_2O_4$ or Na_2SO_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.

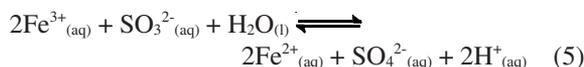**Determination of optimum time:** A standard solution of 100 ppm Fe(III) (0.5 mL) was added into a reducing agent
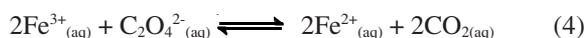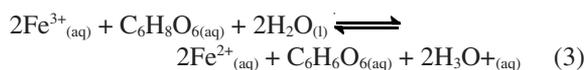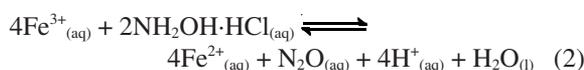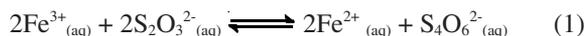
solution. The mixture was added with 1.5 mL acetate buffer at optimum pH. Afterward, the mixture was added with 1.5 mL 1,10-Phenantrolin 1000 ppm and 5 mL of acetone then diluted with deionized water. The variation time for complex formation was measured at 0, 15, 30, 45, 60 min.

Determination of optimum concentration: The treatment for determination of optimum reduction concentration was the same as the treatment of determination of pH optimum for reduction. But, the difference is the concentration of each reducing agent. Data variation concentration of reducing agents is shown in Table-1. After the treatment is carried out until the dilution stage with deionized water, then measured by UV-visible spectrometry.

TABLE-1
CONCENTRATION VARIATION OF REDUCING AGENTS

Variation concentration of reducing agent (ppm)				
$Na_2S_2O_3$	$NH_2OH \cdot HCl$	$C_6H_8O_6$	$Na_2C_2O_4$	Na_2SO_3
5	5	3	10	40
7	6	4	11	50
9	7	5	12	60
11	8	6	13	70
13	9	7	14	80
15	10	8	15	–
–	11	9	–	–
–	12	–	–	–

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, $FeCl_3 \cdot 6H_2O$ 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:

$$2Fe^{3+}_{(aq)} + 2S_2O_3^{2-}_{(aq)} \rightleftharpoons 2Fe^{2+}_{(aq)} + S_4O_6^{2-}_{(aq)} \quad (1)$$

$$4Fe^{3+}_{(aq)} + 2NH_2OH \cdot HCl_{(aq)} \rightleftharpoons$$
$$4Fe^{2+}_{(aq)} + N_2O_{(aq)} + 4H^+_{(aq)} + H_2O_{(l)} \quad (2)$$

$$2Fe^{3+}_{(aq)} + C_6H_8O_{6(aq)} + 2H_2O_{(l)} \rightleftharpoons$$
$$2Fe^{2+}_{(aq)} + C_6H_6O_{6(aq)} + 2H_3O+_{(aq)} \quad (3)$$

$$2Fe^{3+}_{(aq)} + C_2O_4^{2-}_{(aq)} \rightleftharpoons 2Fe^{2+}_{(aq)} + 2CO_{2(aq)} \quad (4)$$

$$2Fe^{3+}_{(aq)} + SO_3^{2-}_{(aq)} + H_2O_{(l)} \rightleftharpoons$$
$$2Fe^{2+}_{(aq)} + SO_4^{2-}_{(aq)} + 2H^+_{(aq)} \quad (5)$$

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.
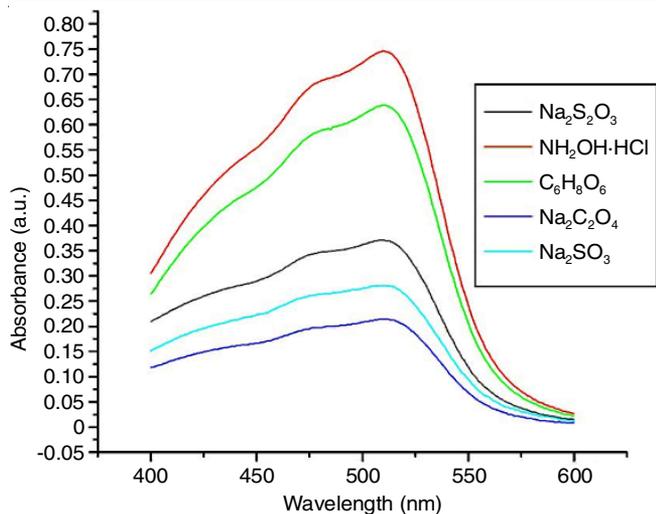
Fig. 1. Wavelength (nm) Fe(II)-phenanthroline with reducing agents

TABLE-2
OPTIMUM pH ACETATE BUFFER FOR REDUCING AGENTS

Reducing agent	pH	Absorbance (nm)
$Na_2S_2O_3$	4.5	0.434
$NH_2OH·HCl$	4.5	0.632
$C_6H_8O_6$	4.5	0.610
$Na_2C_2O_4$	5.0	0.268
Na_2SO_3	4.0	0.280

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-henanthroline, 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-3
OPTIMUM TIME FOR REDUCING AGENTS

Reducing agent	Time (min)	Absorbance (nm)
$Na_2S_2O_3$	15	0.320
$NH_2OH·HCl$	15	0.799
$C_6H_8O_6$	15	0.610
$Na_2C_2O_4$	45	0.268
Na_2SO_3	30	0.406

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 $NH_2OH·HCl$ is 11 ppm and $C_6H_8O_6$ is 7 ppm. But the peak was out of Lambert-Beer range
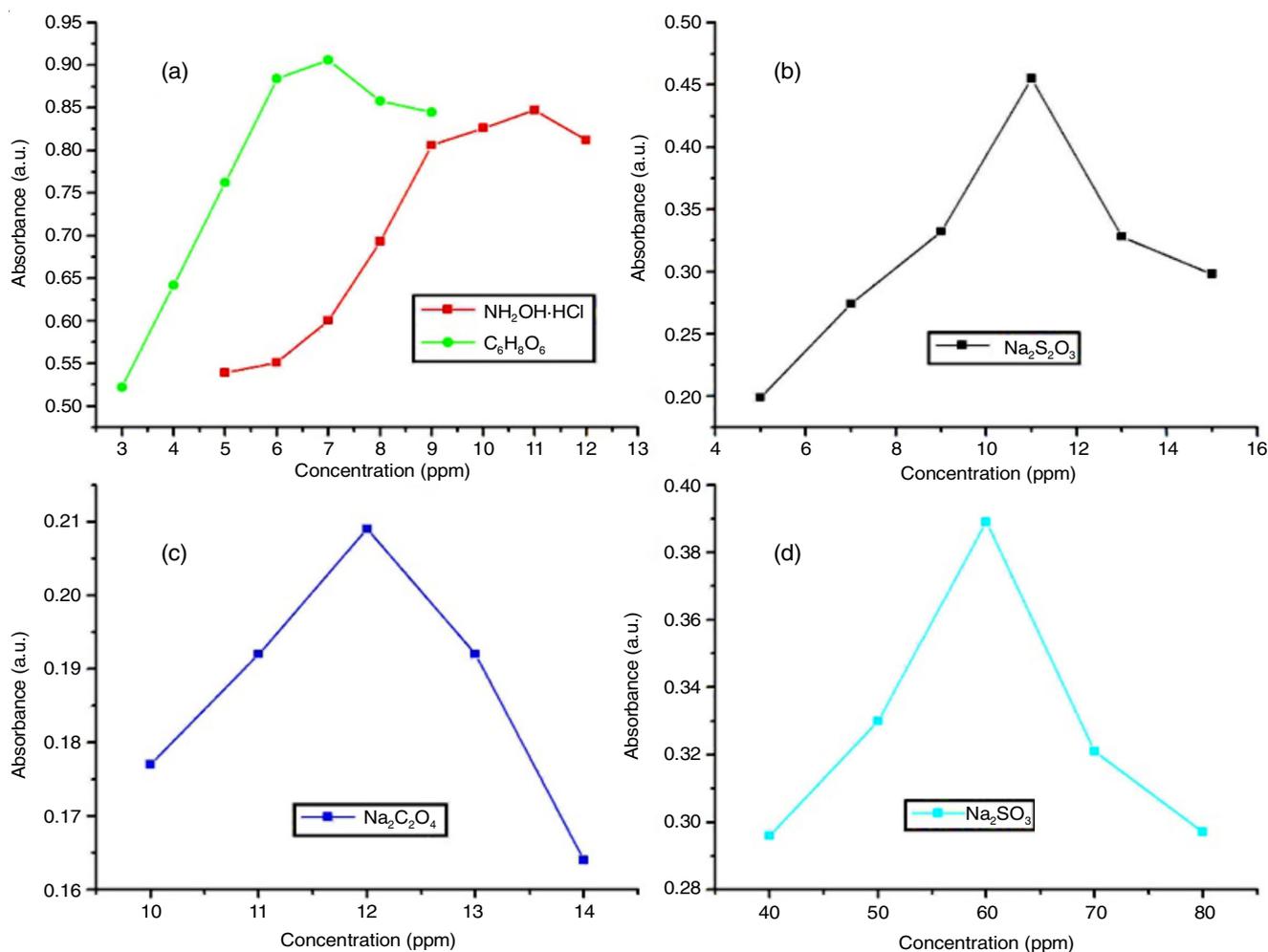

Fig. 2. Optimum curve concentration Fe(II)-phenanthroline with reducing agents

TABLE-4 OPTIMUM REDUCING AGENTS CONCENTRATION		
Reducing agent	Concentration (ppm)	Absorbance (nm)
$Na_2S_2O_3$	11	0.455
$NH_2OH \cdot HCl$	8	0.693
$C_6H_8O_6$	5	0.762
$Na_2C_2O_4$	12	0.209
Na_2SO_3	60	0.389

(0.2-0.8). So, to comply with the regulation, the concentration of $NH_2OH \cdot HCl$ was adjusted to 8 ppm with absorbance 0.693 and $C_6H_8O_6$ 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-5 RECOVERY (%) OF REDUCING AGENTS	
Reductors	Recovery (%)
$Na_2S_2O_3$	103.440
$NH_2OH \cdot HCl$	116.007
$C_6H_8O_6$	98.068
$Na_2C_2O_4$	85.886
Na_2SO_3	84.590

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 ($NH_2OH \cdot HCl$) 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 ($C_6H_8O_6$) 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 $Na_2S_2O_3$), 116.00 % (for $NH_2OH \cdot HCl$), 98.068 % (for $C_6H_8O_6$), 85.97 % (for $Na_2C_2O_4$) and 103.44 % (for Na_2SO_3).

CONFLICT OF INTEREST

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

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