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Flotation, speciation and determination of iron(III) using aluminon in water, real samples and wastes of power stations

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ABSTRACT

Aluminon has been investigated for the separation of iron(III) by flotation technique. This reagent formed a 1:1 stable complex in aqueous solution. An intense violet layer is formed after flotation using oleic acid (HOL). A highly selective and sensitive spectrophotometric procedure is proposed for the determination of Fe(III) after overcoming all interferences. Preliminary studies show the possibility of forming a complex with Fe(II) to an extremely low extent. Trials have been carried out to separate Fe(II) and Fe(III) using NH_4SCN or NaF. To prevent the oxidation of Fe(II), $NaBH_4$ is used. The separation of Fe(III) and Fe(II) can be achieved using 0.6 mg L^{-1} $NaBH_4$. The flotation- determination method was carried out at pH 2-3. The formation constant is 1.3×10^7 L mol^{-1} with molar absorptivity of 0.2×10^5 $Lmol^{-1}$ cm^{-1} and detection limit of 5×10^{-6} $molL^{-1}$. The effect of foreign ions is avoided using excess aluminon and 0.5 mg L^{-1} $NaBH_4$. The proposed procedure was applied to synthetic mixtures [Fe(III) + Fe(II)], Fe(III) and some cations, wastes of power stations, simulated samples and real ores.

1. Introduction

Iron occurs with molybdenum in enzymes that catalyze nitrogen fixation [1]. The preconcentration and determination of iron in different oxidation states are the aim of many workers, especially in environmental chemistry, industrial food, agriculture and pharmaceutical clinical control [2]. In this concern, numerous techniques for the separation and preconcentration of trace metals have been reported [3-8]. Flotation has many advantages owing to simplicity, time saving, non expensive reagents and apparatus and incorporated as a clean technology to treat water and wastewater [9]. Few publications deals with the separation of Fe(III) from Fe(II) [10]. Although the separation of Fe(III) by ion and precipitate flotation [11-16] was carried out, no trial was made to use aluminon in this respect.

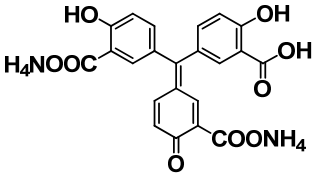
Heavy metal pollution is spreading throughout the world with the expansion of industrial activities [17]. These metals, which find many useful applications, are harmful if they are discharged into natural water resources with serious health hazards [18-20]. In other words, heavy metals which are of great environmental concern must be removed [21-23]. Industrial wastewater contains high levels of heavy metals and to avoid water pollution, treatment is needed before disposal.

In the present work, flotation and speciation of Fe(III) using aluminon and HOL were proposed. Experimental variables were examined. In addition, Fe(III) determination in synthetic, real samples, different water samples and wastes from power stations was carried out.

2. Experimental

2.1. Chemicals and solutions

Unless otherwise stated, all chemicals used in this study were of analytical grade or high purity. Aluminon [$C_{22}H_{23}N_3O_9$ solution [1×10^{-2} mol L^{-1}] (Scheme 1) was prepared by dissolving 0.47 g in 100 mL bidistilled water. Oleic acid [6.36×10^{-2} mol L^{-1}] was prepared by dispersing 20 mL in 1 L kerosene. Fe(III) [1×10^{-2} mol L^{-1}] was taken from the standard solution. Fe(II) [1×10^{-2} mol L^{-1}] was prepared from $FeSO_4.7H_2O$ in 100 mL; the solution must be freshly prepared. A stock solution of 1×10^{-2} mol L^{-1} EDTA was prepared by dissolving 3.74 g in 1 L bidistilled water and standardized. A 0.1 mol L^{-1} of oxalic, HNO_3, NH_4OH and $Pb(NO_3)_2$, each, was prepared by dissolving the calculated weight in 100 mL solution. Diluted concentrations of NaF, NH_4SCN and $NaBH_4$ were prepared from stock solutions of 0.1 mol L^{-1} of NaF, NH_4SCN and 10 mg L^{-1} of $NaBH_4$.



Scheme 1

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2.2. Instrumentation

Two flotation cells were used. The first was a tube of 1.2 cm inner diameter and 29 cm length with a stopcock at the bottom. Such a cell was used during the study of the factors affecting the efficiency of flotation. The second was a cylindrical tube of 6 cm inner diameter and 45 cm length with a stopcock at the bottom and a quick-fit stopper at the top. It was used for the separation of the investigated analyte from a relatively large volume. The spectrophotometric data were recorded on a Unicam UV_2 spectrophotometer. The concentrations of Fe were determined using a Perkin Elmer 2380 Atomic Absorption Spectrometer with air-acetylene flame. The optimum instrumental parameters used are: wavelength: 248.3 nm; lamp current: 25 mA; Fuel flow rate: 3 L min^{-1}; air flow rate: 21 L min^{-1}; burner height: 0.9 cm and slit width: 0.7 nm. The IR spectra of aluminon and its solid complexes were recorded on a Mattson 5000 FTIR spectrophotometer. The pH values of all solutions prepared before flotation were carried out using HANA instrument 8519 digital pH-meter (*Italy*). The mass spectra of the Fe(III) complex was measured at 70 eV with a Varian MAT 311 instrument at National Research Center, Cairo. Magnetic measurements were carried out on a Johnson-Matthey magnetic susceptibility balance, UK. Carbon and hydrogen content for the formed aluminon-Fe(III) complexes was determined at the Microanalytical Unit, Cairo University, Egypt. The Fe analysis was carried out according to the standard methods [24].

2.3. Preparations

Aluminon (Scheme 1) is provided from Riedel-de Haen, Germany. The solid complex, in aqueous solution, was prepared by mixing equimolar amounts of aluminon and Fe(III) ions in H_2O-EtOH solution. The colored solid complex that precipitated was filtered off and dried under vacuum. On the other hand, the complex in the scum layer was obtained by gathering the float layer in some flotation experiments (equimolar amounts of aluminon and Fe(III) ions in presence of 3 mL HOL). The float was filtered, washed with bidistilled water and ethanol, dried in oven at 80 °C and preserved in a desiccator.

2.4. Separation-determination of Fe(III) and Fe(II)

Suitable concentration (2×10^{-5} mol L^{-1}) of Fe(III) and Fe(II), 0.5 mg L^{-1} of $NaBH_4$ and aluminon (2×10^{-4} mol L^{-1}) were introduced into a flotation cell. The pH of the solution was adjusted to ≈ 2 by adding drops of 0.1 mol L^{-1} HCl. The cell was shaken manually for about 2 min, after which 3 mL of 2×10^{-3} mol L^{-1} HOL were added. The cell was then turned upside down many times by hand for complete flotation of Fe(III)-aluminon species. The mother liquor was separated from the flotation cell and then introduced into the AAS flame for measurement of Fe(II). The floatability of Fe(II) was obtained from the relationship:

$$F_{Fe(II)} = \frac{C_i - C_f}{C_i} x100\% \quad (1)$$

C_i and C_f denote the initial and final concentrations of Fe(II). Subsequently, 2 mL of conc. HCl were added to the scum inside the flotation cell and the mixture was shaken thoroughly to extract the Fe(III) from the scum. The extract was made up to a suitable volume having a final concentration of 2×10^{-4} mol L^{-1} of aluminon. The Fe(III) was measured by AAS against a standard Fe(III) solution containing the same concentration of aluminon. The efficiency of flotation of the Fe(III) in the scum was determined from the relationship:

$$F_{Fe(III)} = (C_s/C_i)\times100\% \quad (2)$$

C_s denote the concentration of Fe(III) in the scum. Titrimetric procedure for determination of Fe(III): To a conical flask, add 5 mL of Fe(III) solution, 20 mL bidistilled water, 5 mL of 0.01 mol L^{-1} EDTA, two drops of xylenol orange and hexamine, then titrate against 0.01 mol L^{-1} $Pb(NO_3)_2$ [24].

2.5. Applications

Synthetic mixtures: Into a flotation cell, 1.12 ppm of Fe(III) was taken and strict concentration was added from each foreign ion individually or in combination in presence of 2×10^{-4} molL^{-1} aluminon in Fe(III) separation. The procedures for flotation, separation, elution and spectrophotometric (atomic absorption) determination were carried out.

Natural water samples: To 100 mL aliquot of clean uncontaminated, filtered natural water samples, different concentrations of the investigated analyte were introduced with excess aluminon. The previous procedures of separation and determination were carried out.

Real samples: Lead-zinc sulfide and stream sediment ores [25] were provided from National Center of Metrology. Accurately 0.5 g solid sample was completely dissolved in Teflon beaker with mixture of acids (45 mL HF, 15 mL H_2SO_4 and 5 mL HNO_3). After complete dissolution, the solution was evaporated till dryness. The residue was then dissolved in 20 mL HCl (1:1) and completed to 100 mL in a measuring flask with bidistilled water.

3. Results and Discussion

3.1. Separation and determination of Fe(III)

The separation-flotaion of Fe(III) enabling one to apply this new technique on waste samples taken from the power stations before discharge. This followed by studying the separation of Fe(II) from Fe(III) and modifying an analytical method for determination of both in one sample.

3.1.1. Influence of the hydrogen ion concentration

A series of experiments were carried out to study the effect of pH on the flotation efficiency of Fe(III) [2×10^{-5} mol L^{-1}] with 2×10^{-3} mol L^{-1} HOL in absence and presence of 1×10^{-4} mol L^{-1} aluminon. Figure 1b shows that about 45% is the maximum separation efficiency at pH 2-3. Accordingly, the separation of Fe(III) needs modification. Aluminon imposed itself as a good chelating agent. Figure 1a shows that ≈ 100% efficiency was obtained at pH 2-3. In basic medium, the separation decreases due to the formation of oleate. Direct addition of ferric ammonium sulfate and aluminon acquires pH ≈ 3.

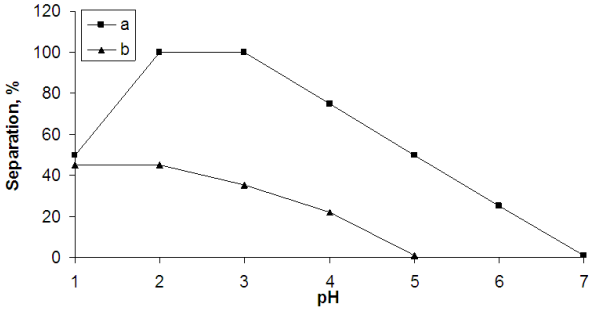


Figure 1. Effect of pH on the separation efficiency of 2×10^{-5} mol L^{-1} Fe(III) using 2×10^{-3} mol L^{-1} HOL without aluminon (curve a) and with 1×10^{-4} mol L^{-1} aluminon (curve b).

3.1.2. Influence of interacting species concentrations

The effect of Fe(III), aluminon and HOL is investigated. Figure 2 show that the floatability of Fe(III) increases reaching 100% at 2×10^{-5} mol L^{-1} aluminon with molar ratio of 1:1 at pH ≈ 3. This simplified the procedure for the analytical separation and determination of Fe(III), specially in samples containing unknown amounts of Fe(III); the selected concentration of aluminon for further experiments was 1×10^{-4} mol L^{-1}.

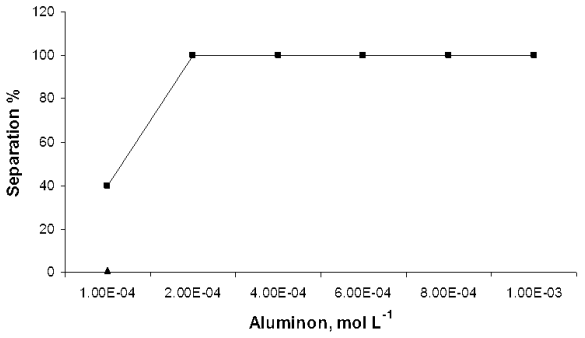


Figure 2. Effect of aluminon concentration on the separation efficiency of 2×10^{-5} mol L^{-1} Fe(III) at pH ≈ 3 using 2×10^{-3} mol L^{-1} HOL.

Figure 3a represents the separation percentage of Fe(III) using 2×10^{-3} mol L^{-1} HOL at pH ≈ 3 in absence of aluminon. The percentage is ≈ 45% and by increasing the analyte concentration, the floatability decreases owing to the presence of insufficient amounts of oleate capable for floating all the present Fe(III) ions. Also, to confirm the data in Figure 2, another series of experiments were carried out to float different amounts of Fe(III) ions. In Figure 3b, the separation percentage achieved 100% corresponding to the 1:1 Fe(III): aluminon ratio.

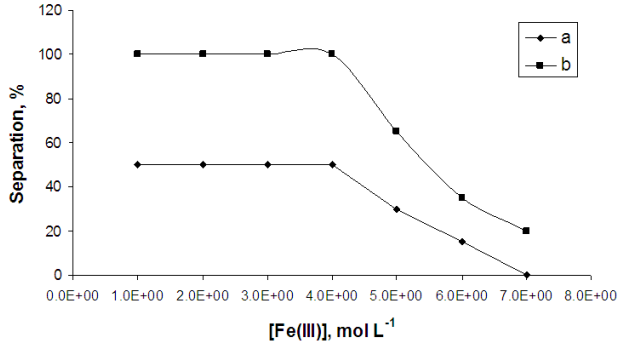


Figure 3. Separation efficiency of different Fe(III) concentrations at pH ≈ 3 in absence (curve a) and presence of 2×10^{-5} mol L^{-1} aluminon (curve b) using 2×10^{-3} mol L^{-1} HOL.

The floatability of Fe(III) at different concentrations of HOL in absence (Figure 4, curve a) and presence (Figure 4, curve b) of aluminon was investigated. Curve (a) shows 45% floatability even at different concentrations of HOL. Curve b shows ≈ 100% floatability of Fe(III) at 10^{-4} mol L^{-1} of HOL and remains constant. Accordingly, 2×10^{-3} mol L^{-1} HOL was used throughout the work.

Spectrophotometric measurements were carried out to assure the data obtained in Figures 2 and 3. The absorption spectra of Fe(III), aluminon and Fe(III)-aluminon systems showed that aluminon and Fe(III) have no absorption bands at the wavelength range of Fe(III)-aluminon. The aqueous complex shows a band centered at 580 nm. The stoichiometry of the complex formed was ascertained applying the continuous variation method. The results revealed the formation of 1:1 [Fe(III)-aluminon] ratio. The apparent formation constant (K_f) of the complex is 1.3×10^{7} L mol^{-1}.

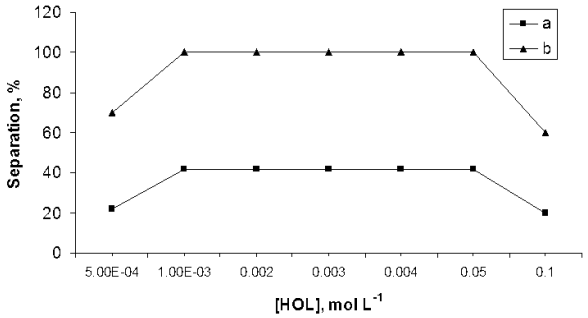


Figure 4. Influence of HOL concentration on the separation efficiency of 2×10^{-5} mol L^{-1} Fe(III) in absence of aluminon (curve a) and in presence of 1×10^{-4} mol L^{-1} (curve b) at pH ≈ 3.

3.1.3. Influence of volume

Series of experiments were conducted to float different quantities of Fe(III) in a fixed volume (10 mL) under the recommended conditions. It was found that the smallest amount of the analyte which can be safely and quantitatively separated from 10 mL is 2×10^{-5} mol L^{-1}. Another series of experiments were conducted to float a fixed concentration of the analyte (2×10^{-3} mol L^{-1}) from different aqueous volumes using suitable large flotation cells under the recommended conditions. The data showed that 1×10^{-3} mol L^{-1} of Fe(III) can be quantitatively separated from different aqueous volumes up to 2 L after which, the floatability decreases by 30% at 2.5 L. Accordingly, the detection limit of separation procedure is 0.56 ppm.

3.1.4. Influence of temperature

Solutions of Fe(III), HOL and aluminon were either heated or cooled. The aluminon and HOL are quickly poured into the Fe(III) solution at zero time. The solution was introduced into flotation cell jacked with 1 cm thick fiberglass insulation at pH ≈ 3. The data indicated that temperature up to 60 °C has no effect on the flotation process. Hence, subsequent experiments were carried out at 25 ± 1 °C.

3.1.5. Influence of ionic strength

The effect of ionic strength on the separation efficiency of Fe(III) under the recommended conditions (Table 1) indicated that, Na^+, K^+, Mg^{2+} and Ca^{2+} as Cl^-, NO_3^-, SO_4^{2-}, NO_2^- and/or I^- added during the flotation separation of the analyte have no effect up to 0.5 mol L^{-1} concentration level.

Table 1. Effect of ionic strength on the separation efficiency of 2×10^{-5} mol L^{-1} Fe(III) using 2×10^{-4} mol L^{-1} aluminon and 2×10^{-3} mol L^{-1} HOL at pH ≈3.

Cation*	Concentration, mol L^{-1}	Recovery, %
	0.50	99.8
Na^+	0.10	99.9
	0.05	99.9
	0.50	98.9
K^+	0.10	98.9
	0.05	99.5
	0.50	99.5
Mg^{2+}	0.10	99.5
	0.05	99.7
	0.50	98.8
Ca^{2+}	0.10	98.8
	0.05	99.4

* Na^+, K^+, Mg^{2+} and Ca^{2+} were taken as Cl^-, SO_4^{2-} or NO_3^-.

3.1.6. Effect of foreign ions

The data presented in Table 2 showed that, the investigated interfering ions up to 50 mg L^{-1} (each) individually or in combination have no pronounced effect on the separation efficiency of Fe(III) even on using 2×10^{-4} mol L^{-1} aluminon. The interfering species present with Fe(III) depress the separation efficiency; excess aluminon overcome this effect.

Table 2. Effect of some foreign ions individually or in combinations on the separation efficiency of 2×10^{-5} mol L^{-1} of Fe(III) in presence of different aluminon concentrations using 2×10^{-3} mol L^{-1} HOL at pH ≈3.

Foreign ion(s)	Concent., mg L^{-1}	Recovery %	
		Using 1×10^{-4} mol L^{-1} aluminon	Using 2×10^{-4} mol L^{-1} aluminon
Cu(II)	1000	100.0	100.0
Pb(II)	1000	99.5	99.9
Ni(II)	1000	99.8	99.9
Hg(II)	1000	99.7	99.9
Ca(II)	1000	99.9	100.0
Ag(I)	500	99.9	99.9
Li(I)	500	99.9	100.0
La(III)	500	99.7	99.8
Cd(II)	500	99.8	99.9
Mg(II)	500	99.7	99.9
Te(II)	500	99.8	99.9
Mn(II)	500	60.0	100.0
Sr(II)	100	99.9	100.0
Co(II)	100	85.0	100.0
Al(III)	100	80.0	100.0
Th(IV)	50	99.7	99.8
W(III)	50	99.8	99.9
V(IV)	50	99.6	99.8
Cr(III)	50	99.7	99.8
Mo(III)	50	99.8	99.9
Sn(IV)	50	99.8	99.9
In(III)	50	99.7	99.8
As(III)	50	99.9	99.9
Zn(II)	50	75.0	99.9
Zr(IV)	50	69.0	99.9
Cu(II)+Mg(II)	500	99.7	99.8
Cu(II)+Ca(II)	500	99.9	100.0
Ni(II)+Ag(I)	500	99.8	99.9
La(III)+Ti(IV)	500	99.8	99.9
Cu(II)+Ca(II)+Mg(II)	500	99.7	99.8
Cu(II)+Ca(II)+Hg(II)	500	99.8	99.9
Cd(II)+Ca(II)+La(III)	500	99.8	99.9
Ni(II)+Pb(II)+Li(I)	500	99.7	99.8
Te(II)+Mg(II)+La(III)	500	99.8	99.9
Cu(II)+Sr(II)	100	99.9	99.9
Co(II)+Sr(II)	100	80.0	99.9
Al(III)+Th(IV)	50	99.8	99.9
Cu(II)+W(III)	50	99.7	99.9
Cu(II)+Cr(III)+Zn(II)	50	75.0	99.9
Zn(II)+V(IV)+Ni(II)	50	80.0	99.8

3.2. Separation of Fe(II) from Fe(III)

None of the freshly prepared Fe(II) that exposed to air gave results different from that of less exposed; freshly prepared is also studied. The same previous results are obtained, but with slight decrease in flotation. This observation leads to think that aluminon can oxidize part of Fe(II) to Fe(III) forming Fe(III) complex until all Fe(II) are oxidized. The process is followed sequentially till all Fe(II) is complexed completely. The data depicted in Figure 5 showed zero separation up to 25 min and increases gradually reaching 100% in 1 h. Complete separation and oxidation of Fe(II) within 1 h is due to its little concentration (2×10^{-5} mol L^{-1}). The separation of Fe(II) was carried out within 25 min. Also, the spectral measurements confirm that freshly prepared Fe(II) was not floated even in the presence of aluminon which may be due to the unstability of Fe(II) – aluminon complex. Consequently, the isolation of Fe(II) must be carried out in absence of air.

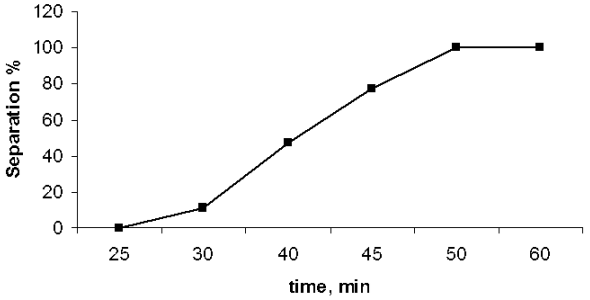


Figure 5. Effect of time on the separation percentage of 2×10^{-5} mol L^{-1} Fe(II) at pH ≈ 3 in presence of 1×10^{-4} mol L^{-1} aluminon and 2×10^{-3} mol L^{-1} HOL.

Trials to separate Fe(II) / Fe(III) using NH_4SCN or NaF have been carried out. Figure 6 shows the influence of NaF on the separation speciation in which there is a gradual increase in the separation curve of Fe(II) due to partial oxidation with time forming a complex giving a maximum at 25%. On the other hand, the separation curve of Fe(III) decreases gradually due to its existence as unfloated $[FeF_6]^{3-}$. So, Fe(III)-aluminon, $[FeF_6]^{3-}$ and oxidized Fe(II) reflect incomplete separation.

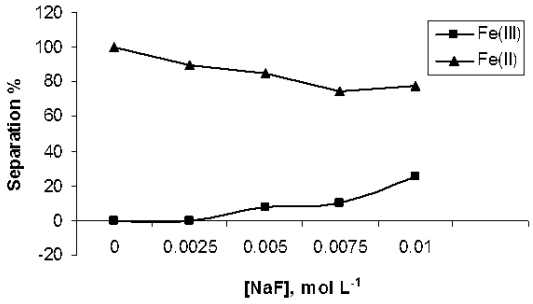


Figure 6. Effect of [NaF] on the separation efficiency of a mixture (2×10^{-5} mol L^{-1}) of Fe(III) and Fe(II), (2×10^{-5} mol L^{-1}) each, in presence of 2×10^{-4} mol L^{-1} aluminon using 2×10^{-3} mol L^{-1} HOL at pH ≈ 3.

The data obtained in the presence of NH_4SCN showed a decrease in the separation of Fe(III) due to the presence of Fe(III)–aluminon and Fe(III)-thiocyanate complexes. The separation of Fe(II) increases up to 40% due to partial oxidation of Fe(II) forming Fe(III)–aluminon and Fe(III)-thiocyanate. The incomplete separation is due to the presence of Fe(III)-thiocyante float and the already formed Fe(III)-aluminon and the oxidized part of Fe(II). So, the separation is not selective. Trials to achieve complete separation of Fe(III) from Fe(II) were carried out by the previous two experiments using equal concentrations of Fe(III), aluminon and Fe(II), (2×10^{-5} mol L^{-1}) each, using 2×10^{-3} mol L^{-1} HOL at pH ≈ 3 in presence of NaF or NH_4SCN. The ratio of 1:1 (Fe(III)-aluminon) assure that all aluminon reacted with Fe(III) and nothing with the partially oxidized Fe(II).

The trials focused on using $NaBH_4$ with different concentrations to show the effect of time on the separation percentage of 2×10^{-5} mol L^{-1} Fe(II) in the presence of 1×10^{-4} mol L^{-1} aluminon and 2×10^{-3} mol L^{-1} HOL at pH ≈ 2. The separation was still zero up to 25 min by adding 0.5 mg L^{-1} $NaBH_4$ meaning that Fe(II) is not oxidized. The data showed complete separation of Fe(III) up to 0.6 mg L^{-1} $NaBH_4$. The separation of Fe(III) decreases after 0.6 mg L^{-1} $NaBH_4$ indicating partial reduction of Fe(III) to Fe(II). Figure 7 showes the effect of $NaBH_4$ concentrations on the separation of Fe(II) and Fe(III), 2×10^{-5} mol L^{-1} each, in presence of 2×10^{-4} mol L^{-1} aluminon using 2×10^{-3} mol L^{-1} HOL at pH ≈ 3. In Fe(II) the separation was still zero up to 0.6 mg L^{-1} $NaBH_4$ and increases due to partial oxidation. In conclusion, the mixture of Fe(III)/Fe(II) was separated using 0.6 mg L^{-1} $NaBH_4$ after adjusting the optimum conditions.

Table 3. Simultaneous separation and determination of equal and different concentrations of Fe(III) and Fe(II) covering the range from 2×10^{-5} – 5×10^{-4} mol L^{-1} (1.12–27.9 mg L^{-}) in the presence of 0.5 mg L^{-1} $NaBH_4$, 2×10^{-4} mol L^{-1} aluminon and 2×10^{-3} mol L^{-1} HOL at pH ≈2 *.

Ion	Concentration, mg L^{-1}		AE	RE	SD	Δ	Mean recovery, %
	Added	Found					
Fe(III)	1.12	1.10	-0.02	-1.79	0.016	1.400	100±0.02
Fe(II)	1.12	1.13	0.01	0.89	7.070×10^{-3}	0.600	100±0.01
Fe(III)	2.79	2.77	-0.02	-0.72	7.07×10^{-3}	0.570	100±0.01
Fe(II)	2.79	2.79	0.00	0.00	0.016	0.250	100±0.01
Fe(III)	5.58	5.59	0.01	0.179	0.010	0.179	100±0.01
Fe(II)	5.58	5.57	-0.01	-0.179	0.010	0.179	100±0.01
Fe(III)	1.12	1.14	0.02	1.79	7.070×10^{-3}	0.600	100±0.02
Fe(II)	5.58	5.56	-0.02	-0.36	0.017	0.300	100±0.02
Fe(III)	2.79	2.77	-0.02	-0.70	0.030	1.100	100±0.02
Fe(II)	5.58	5.58	0.00	0.00	0.010	0.180	100±0.01
Fe(III)	1.12	1.11	-0.01	-0.89	0.020	1.790	100±0.01
Fe(II)	27.90	27.70	-0.02	-0.07	0.020	0.070	100±0.01

* AE: Absolute error; RE: Relative error; SD: Standard deviation.

Table 4. Separation and determination of Fe(III) and Fe(II) from synthetic mixtures containing different interferents using 2×10^{-4} mol L^{-1} aluminon, 0.5 ppm $NaBH_4$ and 2×10^{-3}mol L^{-1} HOL at pH ≈2 *.

Synthetic mixture, 100 ppm for each element	Ion	Analyte, mg L^{-1}		AE	RE	SD	Δ	Mean recovery, %
		Added	Found					
Cu(II)+Pb(II)+Ni(II)	Fe (II)	1.12	1.10	-0.02	-1.79	0.017	1.50	100±0.02
	Fe (III)	1.12	1.09	-0.03	-2.70	7.070×10^{-3}	0.60	100±0.01
Hg(II)+Ca(II)+Te(II)	Fe (II)	1.12	1.12	0.00	0.00	0.010	0.89	100±0.01
	Fe (III)	1.12	1.14	0.02	1.79	7.070×10^{-3}	0.60	100±0.01
Pb(II)+Ag(I)+Cd(II)	Fe (II)	1.12	1.13	0.01	0.89	0.010	0.89	100±0.01
	Fe (III)	1.12	1.14	0.02	1.79	0.010×10^{-4}	8.90×10^{-3}	100±0.01
La(III)+Cd(II)+Mg(II)	Fe (II)	1.12	1.10	-0.02	-1.79	0.020	1.89	100±0.02
	Fe (III)	1.12	1.11	-0.01	-0.89	5.000×10^{-5}	4.46×10^{-3}	100±0.01

* AE: Absolute error; RE: Relative error; SD: Standard deviation.

Table 5. Analysis of Fe(III) in real samples at the recommended conditions *.

Sample	Analyte, %		AE	RE	SD	Δ
	Certified	Found				
1-Lead-Zinc sulfide ore.	6.09	6.090	0.000	0.000	0.010	0.16
2-Stream Sediment	19.71	19.713	0.003	0.020	0.010	0.05

* AE: Absolute error; RE: Relative error; SD: Standard deviation.

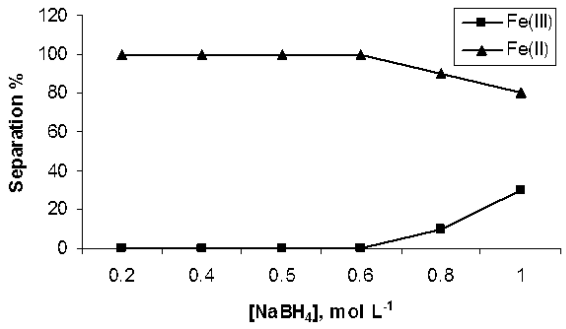


Figure 7. Effect of [$NaBH_4$] on the separation efficiency of a mixture of 2×10^{-5} mol L^{-1} Fe(III) and Fe(II), each in presence of 2×10^{-4} mol L^{-1} aluminon using 2×10^{-3} mol L^{-1} HOL and at pH ≈ 2.

3.3. Applications

Accurate and precise procedure for AAS determination of Fe(III) depends on the formation of a deep violet color in the aqueous layer obeying Beers' law. The molar absorptivity was found to be 0.2×10^{5} L mol^{-1} cm^{-1}. Also, the concentration is easily detected in the aqueous layer (instrumental detection limit is 5×10^{-6} mol L^{-1}) then making a flotation to this colored complex using HOL. This was achieved by an experiment carried to separate 2×10^{-5} mol L^{-1} Fe(III) under its optimum conditions in the scum layer from 2×10^{-5} mol L^{-1} Fe(II) in the mother liquor. After separation, Fe(III) content in the scum layer and Fe(II) content in the mother liquor were determined using FAAS.

The proposed procedure was successfully applied to two synthetic mixtures of Fe(III) and Fe(II) with different concentrations. These were introduced into the flotation cell as a method for the separation of Fe(III) and aspirated into AAS Spectrometry for Fe(III) determination against standard Fe(III) solutions covering the range of 2×10^{-5} – 5×10^{-4} mol L^{-1} (1.12–27.9 ppm) of Fe(III), Table 3. The procedure was applied to the separation and determination of definite Fe(III) concentration in four synthetic mixtures containing Fe(III) and some cations (Table 4). Analysis of Fe(III) in real samples under the recommended conditions was shown in Table 5. Known amount of Fe(III) was added to different water samples and examined by such procedure (Table 6).

3.4. Separation mechanism of Fe(III)

Many experimental studies were carried out to approach the proposal mechanism. These data can be summarized in the following points:

(i) The elemental analysis [C: 39.9 (Found 39.9); H: 4.1 (4.1) and Fe: 8.4 (8.3)] and the mass spectrum (Figure 8) of the complex isolated in aqueous layer indicating that the complex has the formula $[Fe(L)(H_2O)_2SO_4]$.

(ii) The floated species have the same color (violet) as that isolated in aqueous solution.

(iii) The isolated complexes have the same melting points.

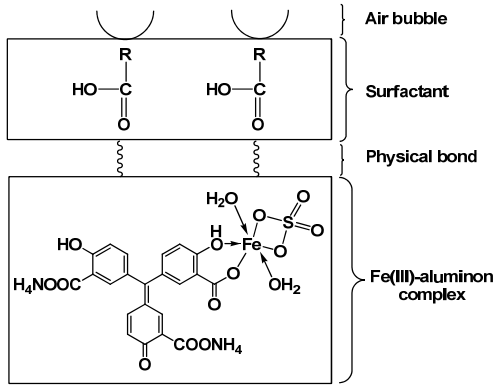
(iv) The two complexes have μ_{eff} ≈ 5.6 BM confirming an octahedral structure [26] around the ferric ion. This geometry is also confirmed by reading the electronic spectra of the two complexes. The spectra show the same band (580 nm) but with different intensities.

Table 6. Recovery of 0.5×10^{-4} and 1×10^{-4} mol L^{-1} of Fe(III) added to some natural water samples delivered from different locations after separation flotation using 1×10^{-3} mol L^{-1} of aluminon and 2×10^{-3} mol L^{-1} HOL at pH ≈3.

Type of water, location*	Analyte added $\times10^{-4}$ mol L^{-1}	Mean recovery
Bidistilled water	0.5	100±0.01
	1.0	100±0.01
Domestic water	0.5	100±0.01
	1.0	100±0.2
Tank water	0.5	105±0.5
	1.0	106±0.3
Sea water, Marsi-Matroah	0.5	105±0.5
	1.0	106±0.4
Sea water, Ras-Elbar	0.5	108±0.2
	1.0	107±0.4
Sea water, Gamasa	0.5	105±0.3
	1.0	105±0.3
Sea water, Al-Areash	0.5	104±0.4
	1.0	105±0.5
Nile water, Mansoura city	o.5	112±0.1
	1.0	109±0.2
Nile water, Talka city (near the power station)	0.5	129±0.5
	1.0	130±0.5
Nile water, Damiatta city (near the power station)	0.5	128±0.5
	1.0	131±0.5
Waste water, Talkha power station		
(a)	1.0	160±0.6
(b)	1.0	150±0.5
(c)	1.0	145±0.7
(d)	1.0	125±0.8
Waste water, Demiatta power station		
(a)	1.0	140±0.8
(b)	1.0	125±0.8
(c)	1.0	138±0.9
(d)	1.0	150±0.9

* a, b, c and d: different samples at different mean times (about one month) from the same location.

(v) The IR spectral bands for all coordination sites are similar. The band at 1240 cm^{-1} is due to $\nu(SO_4)$ [27] and that at 530 cm^{-1} is due to (M-O) [28]. It is concluded that the mechanism of flotation proceeds through physical adsorption with the aid of air bubbles. Accordingly, the floated complex structure may be suggested as shown in Scheme 2.



Scheme 2

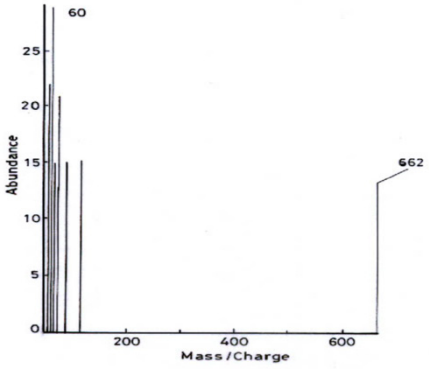


Figure 8. Mass spectrum of Fe(III)-aluminon complex.

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