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Cairo, Egypt

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FORMATIOM OF IRON-DESFERRIOXAMINE COMPLEX AND ITS GAMMA RADIOLYSIS

M.M.EL-DESSOUKY*, A.A.BARAKA*, M.W.ABDEL-RAOUF**

ABSRTRACT

Iron(III) formed a 1:1 complex with desferrioxamine (30-amino-3,14,25-trihydroxy - 3,9,14,20,25 - penta – azatricontance - 2,10,13,21,24 - pentaone methane sulphonate) at pH 5, 7 and 9 with apparent stability constants of $4.4x10^5$, $3.5x10^5$ and $1.8x10^5$ respectively. The complex formed showed stability with time. Amine groups may account for coordination as indicated through IR investigation. Gamma irradiation of formed complex caused its degradation by different amounts at different pH values. Irradiated complex showed no great degradation on standing.

KEY WORDS

Desferrioxamine (abbreviation (D)) , Iron(III), Complex stability, Radiolysis.

INTRODUCTION

Sources of radioactive contamination are many. The detonation of nuclear weapons releases radioisotopes that are called fallout. Fine radioactive dust settles on ground, unprotected personnel, food, water, and equipment. Fallout consists of three types of radioactive materials; fission products, neutron-induced radioisotopes from soil and nuclear bomb components, and non-fission materials that are mostly alpha emitters[1]. Release from phosphorescent materials, calibration instruments, check sources, and training devices are considered as additional sources of radioactive contamination. Radioisotopes are present in the solid, liquid, and gaseous states. Despite the fact that these sources are sealed, they may develop leaks. The leakage of radioactivity may result from deterioration, an accident, damage, poor manufacture, or enemy action. Nuclear accidents while transportation or even storage cause contamination especially when explosion or burning occurs and in this case contamination would be in the metallic form or oxides. Many nuclear power or research reactors are releasing radioactive contamination to environment during their operation. Laboratories that use the radioisotopes for research and medical investigations are considered also as sources of radioactive contamination[1].
Radioisotopes released from the above sources can cause internal contamination through wounds, ingestion, or by inhalation. Each isotope has its own affinity towards certain organ or tissue in which it accumulates and causes harmful radiation effects[2]

* Egyptian Armed Forces.
** Nuclear Energy Authority, Cairo, Egypt.

Fission of nucleus is always asymmetric, producing unstable fragments that are neutron rich, and as a result they decay emitting a sequence of β^- and γ-rays. Some of these fission products are transition elements, lanthanides and actinides, therefor removal of these elements, such contamination, by known drugs is vital[3,4].

EXPERIMENTAL

The experimental work has been carried out at laboratory temperature (20±5°C) in triplicates. Glasswares were thoroughly cleaned by chromic acid and then by distilled water before use. All chemicals used in this study were of high analytical grade. Chloride salt of iron(III) and desferrioxamine ,which paid as pure drug from a drug store, were of high analytical grade. Stock aqueous solution of Fe(III) was prepared with concentration of 10^{-2} M. The same concentration of the chelating agent was prepared. Sartorius analytical balance was used for weighing. FISHER pH meter model 230A is used for pH measurements.

All the optical densities of the solutions were measured using Shimadzu UV visible spectrophotometer UV160. The range of the set is from 1100 to 200 nm. Quartz cells of 1cm light path were used. IR spectra of the crystals of dried samples were taken by ATI unicam FTIR. Continuous variation method was used to determine the composition of the formed complex and to investigate the stability constants of the formed complexes. The absorbance spectra of a complex were investigated at different pH values. The wavelength for measurement was chosen so to display the corresponding peaks. For IR investigation the samples were prepared as solution and dried under IR lamp. The crystals are then used for IR measurements. The range taken was from 4000 to 400 nm.

RESULTS AND DISCUSSION

Figure(1) demonstrates the spectra of Fe(III), desferrioxamine [5,6] of 0.5 x 10^{-2} M, and Fe(III)-D of 0.25 x 10^{-2} M at pH 5,7,and 9 in the range from 300 to 600 nm.

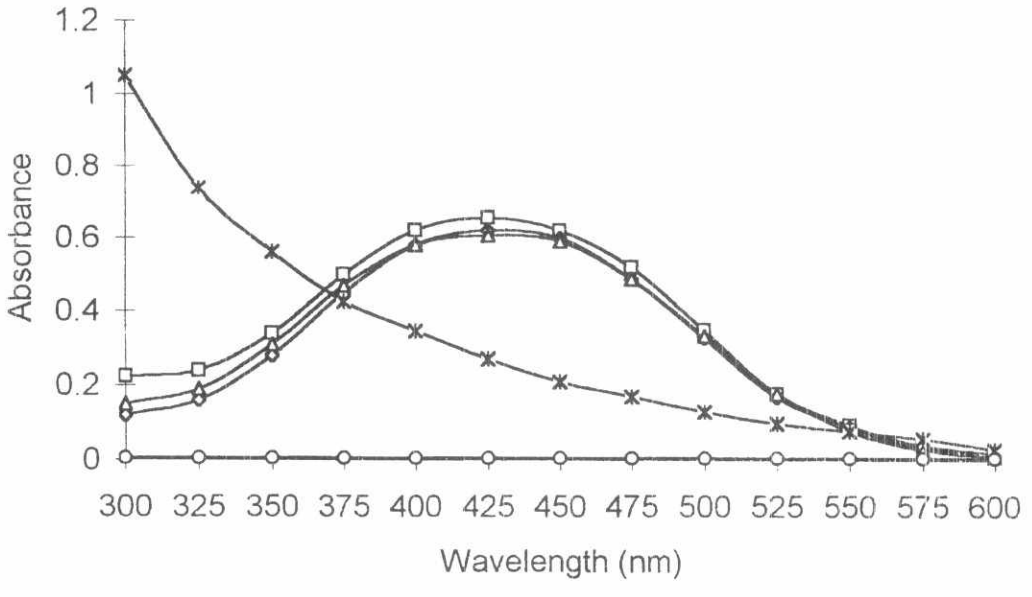


Fig. 1 Spectra of 0.5 x 10^{-2} M Fe(III)(✱), 0.5 x 10^{-2} M Desf.(○) and 0.25 x 10^{-2} M Fe(III)-D complex at pH 5(□), 7(◇) and 9(△).

It shows that Iron(III)-Desferrioxamine (abbreviated; Fe(III)-D) gives peak at 426 nm with no peaks for desferrioxamine and Fe(III) in the range of spectrum under study.

From figure(1) the highest absorbance was for the complex formed at pH 5 with decrease of absorbance for complex formed at pH 7, and 9 of the order 5%, 7.3% respectively. There is no change in λ_{max} as pH changed. This is summarized in table(1).

Table 1 Effect of pH on absorbance of Fe(III)-D complex:

pH	Absorbance
5	0.654
7	0.620
9	0.606

Figure(2) shows absorption spectra of Fe(III)-D complex for different values of chelation ratio, f, at pH 5,7 and 9. The absorbance is maximum for f=0.5 (Fe(III)-D=1:1) for pH values 5,7 and 9.

Figure(3) give the variation of optical absorbance A at λ_{max} with f for Fe(III)-D complex at pH 5,7 and 9 showing molecular ratio metal : desferrioxamine ;M:D=1:1. From the curves of figure(3) and equation(1) the apparent stability constant of complex was calculated and summarized in table(2) [7]. From the table the most stable complex formed at pH 5 then at pH 7 and finally at pH 9.

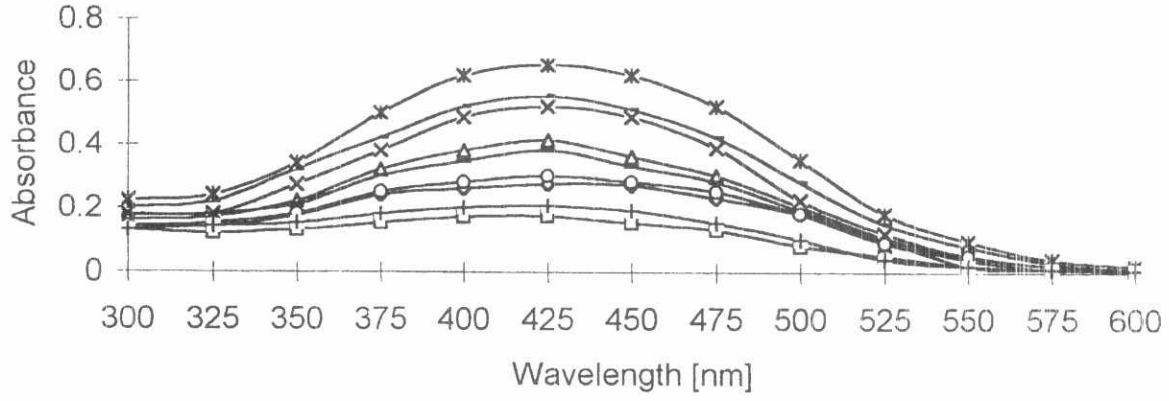
$$K' = \frac{[ML]}{[M][L]} = \frac{(A/A')*C}{(\Delta A/A')*C*(\Delta A/A')*C} = \frac{A/A'}{C*(\Delta A/A')^2} \qquad (1)$$

Where [ML] is the concentration of the complex formed, [M] is the concentration of metal (Iron(III)) and [L] is the concentration of chelating agent; desferrioxamine. A` is the limiting absorbance, A is the actual absorbance, $\Delta A$ is the difference between A` and A. C is the concentration of formed complex which can be deduced from the initial concentration of metal or chelating agent at considered chelation ratio f.

Table 2 Apparent stability constants of Fe(III)-D complexes at pH values 5,7 and 9:

pH	Apparent stability constant $k'_{Fe(III)-D}$
5	4.4×10^5
7	3.5×10^5
9	1.8×10^5

(a)



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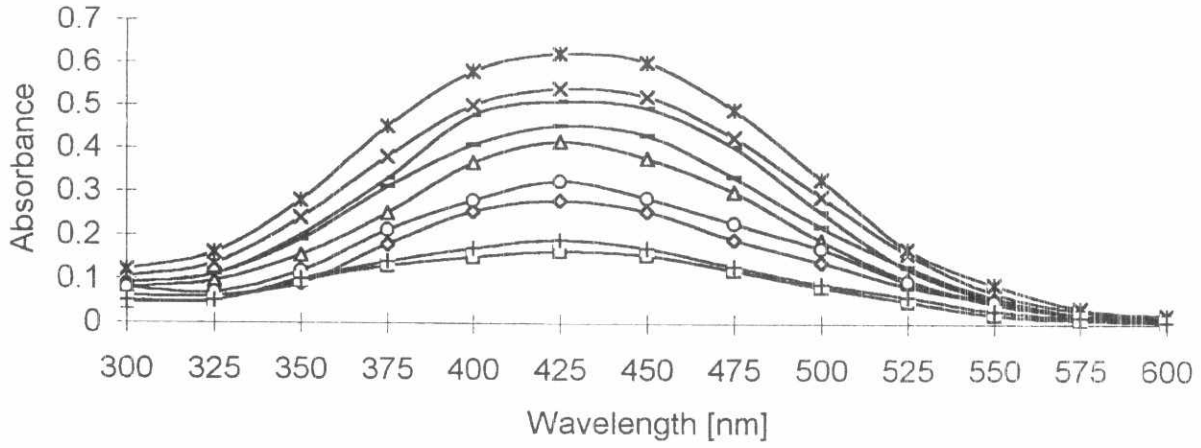

(c)

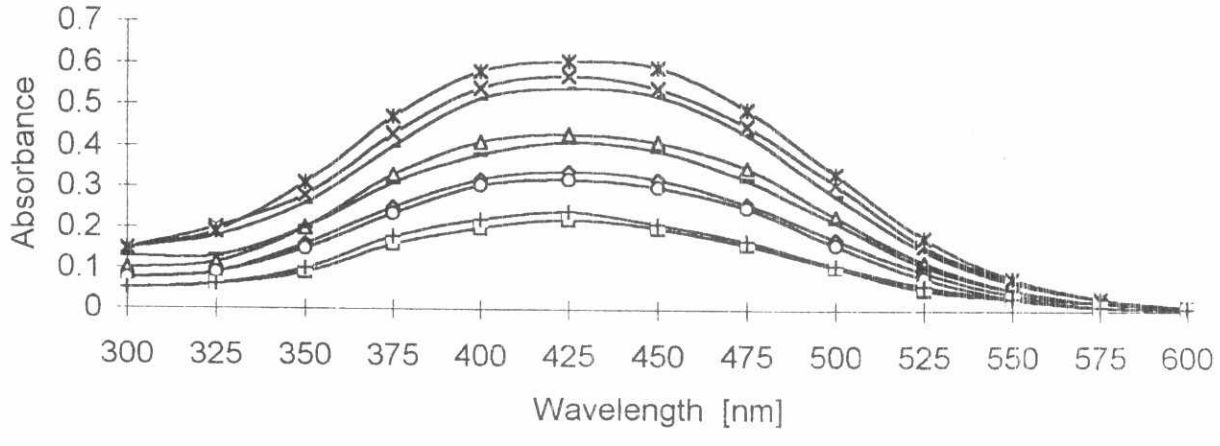

Fig 2 Absorption spectra of Fe(III)-D complex for different values of f at pH 5(a), pH 7(b) and pH 9(c) denoting for f=0.1(-□-),f=0.2(-◊-),f=0.3(-Δ-), f=0.4(-x-),f=0.5(-*-),f=0.6(-),f=0.7(--),f=0.8(-O-),f=0.9(-+-)

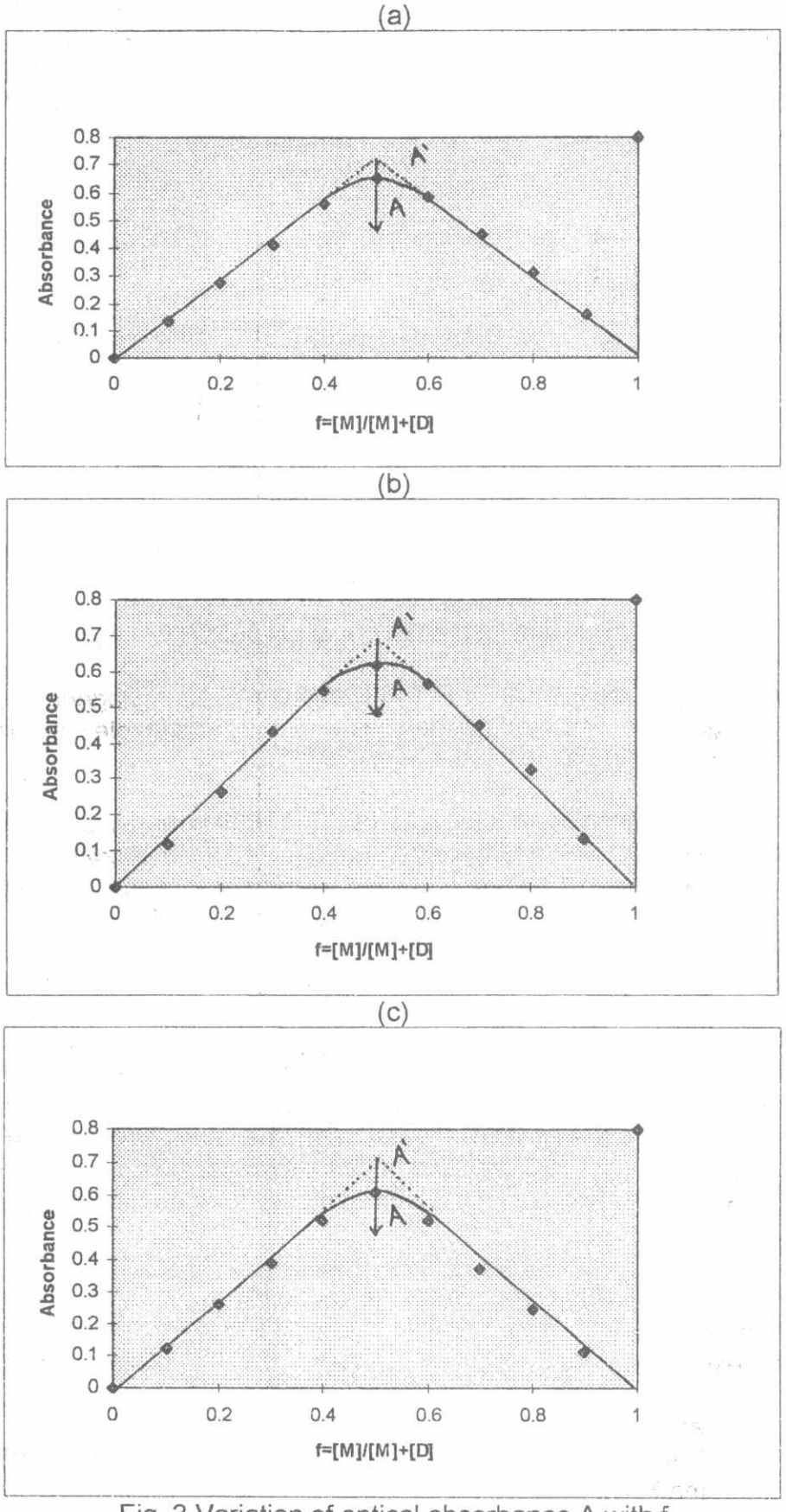

Fig .3 Variation of optical absorbance A with f
at λ_{max} = 426 nm for Fe(III)-D at pH 5(a),7(b),and 9(c)

The aging effect on the formed complex was studied by leaving samples of maximum absorbance at room temperature and measuring them at λ_{max} after several intervals (2 days interval for total period of 10 days). Figure(4) shows that aging has no effect or complexes prepared at different pH values indicating its stability during this tested period.

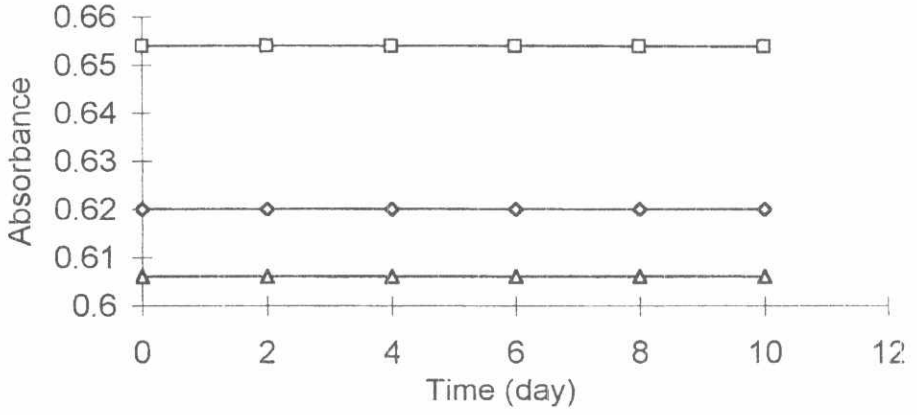

Fig. 4 Aging effect on Fe(III)-D complex
measured at λ_{max} =426 nm at pH 5(□),7(◊)and 9(Δ).

The comparison of IR spectra for Fe(III)-D and chelating agents is shown in figure(5). The basic changes occurred to the spectra of the complex are described relative to that of desferrioxamine as follows:

At pH 5; $-NH_2$ stretching at 3350 cm^{-1} became weaker and splitted. –NH bending at 1560 shifted to 1500 cm^{-1} and became stronger. –C-N vibration at 1310 cm^{-1} became stronger and shifted to 1250 cm^{-1}. –C-N stretching at 1020 cm^{-1} shifted to 1000 cm^{-1}. –NH deformation at 750 cm^{-1} disappeared. New peaks at 680 and 450 cm^{-1} appeared and can be due to coordination with desferrioxamine. At pH 7; $-NH_2$ stretching at 3330 cm^{-1} shifted to 3400 cm^{-1} and became stronger. –NH deformation at 1570 cm^{-1} shifted to 1500 cm^{-1} and became stronger. –CN stretching at 1100 cm^{-1} shifted to 1050 cm^{-1} and became stronger. –NH deformation at 650 cm^{-1} became stronger. New peak near 400 cm^{-1} appeared. At pH 9; $-NH_2$ stretching at 3310 cm^{-1} became weaker. –NH deformation and bending at 1600 cm^{-1} and 1500 cm^{-1} respectively became weaker. -CN vibration at 1310 cm^{-1} became stronger. –CN stretching at 1100 cm^{-1} shifted to 1160 cm^{-1} and became stronger. The discussion suggests that coordination with desferrioxamine occurred mostly through amine groups[8,9].

Irradiation of the formed complexes is important to study its resistance towards radiation and to see if it is capable to stand till removal through urine. Samples of complexes were exposed to a series of doses; 200, 400, 600, 800 and 1000 krad.

At the same range of spectrum used for non-irradiated Fe(III)-D, the spectra of irradiated samples were taken with the same pH values and absorbances were taken at the same λ_{max}.

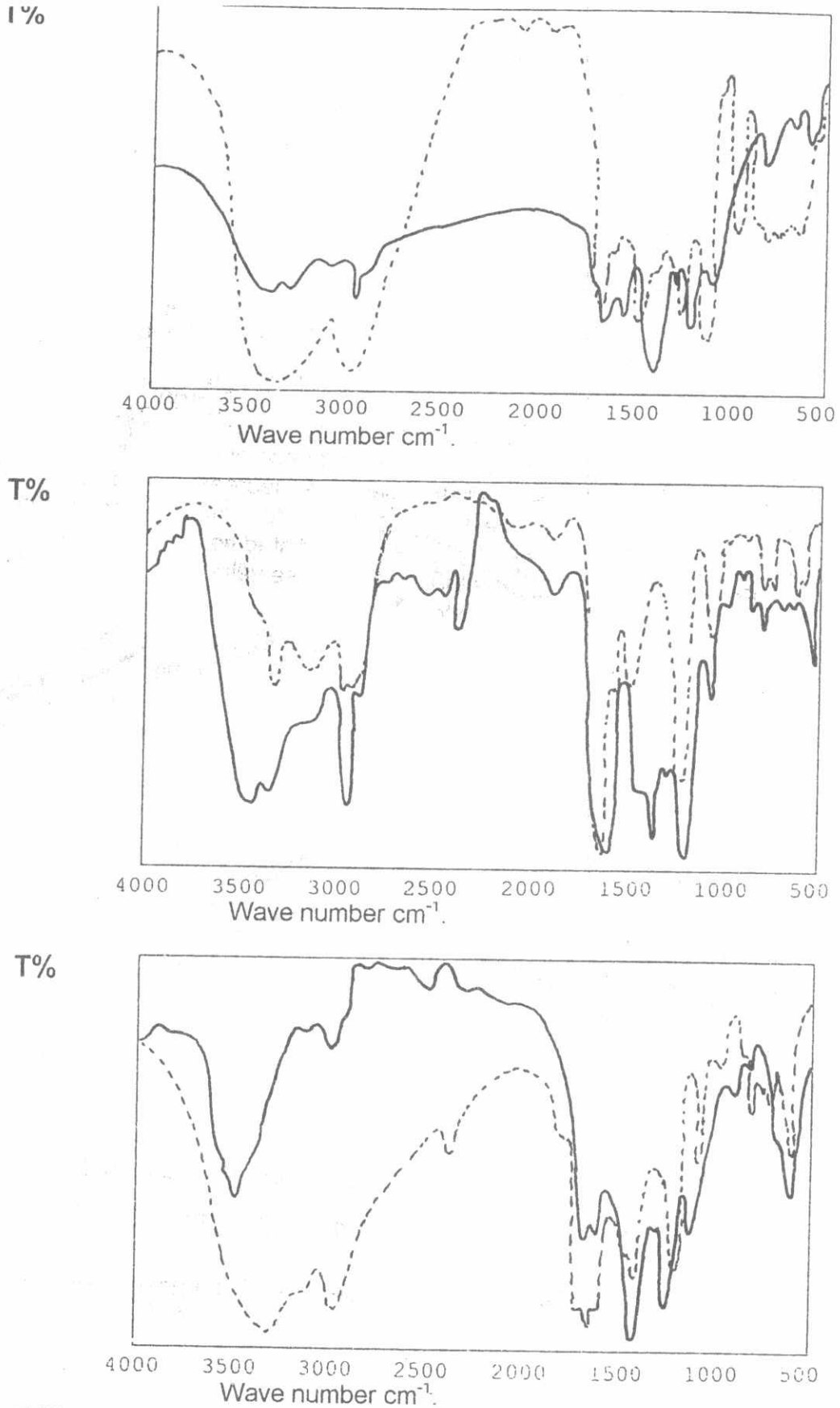

Fig. 5 IR spectra of Desferrixamoine(----)and Fe(III)-D chelate(—) at pH 5(a), pH 7(b), and pH 9(c).

The main species resulting from irradiation of water can be represented as follows:

$$H_2O \rightarrow e^-_s , H^{\cdot} , H_2 , OH^{\cdot} \text{ And } H_2O_2$$

Radiation yield , G-value, which represent formation of these species were previously determined[10] and found to be 0.7, 0.45, 2.7, 2.7 and 0.8 respectively. It is postulated that $OH^{\cdot}$ radical has bigger probability to attack the chelates causing their degradation[11-12]. The reaction rate of $OH^{\cdot}$ radical with chelate is much faster than that of hydrated electrons and hydrogen atom[11,12].

Figure(6) displays the spectra of irradiated Fe(III)-D through the doses under study at pH 5. From table(3), as dose increased the complex breaks down but absorbance still with comparable percentage with respect to non-irradiated samples. The irradiated sample by 1000 Krad gave absorbance of 57% of that of non-irradiated one. The pH values of the irradiated samples decreased approximately by 0.5. Figure(7) demonstrates the spectra of samples for different doses after 20 days. Table(4) summarizes the effect of age on irradiated samples through absorbances and pH. From the table it appears that at each dose value the absorbance decreased and pH value increased to a little extent.

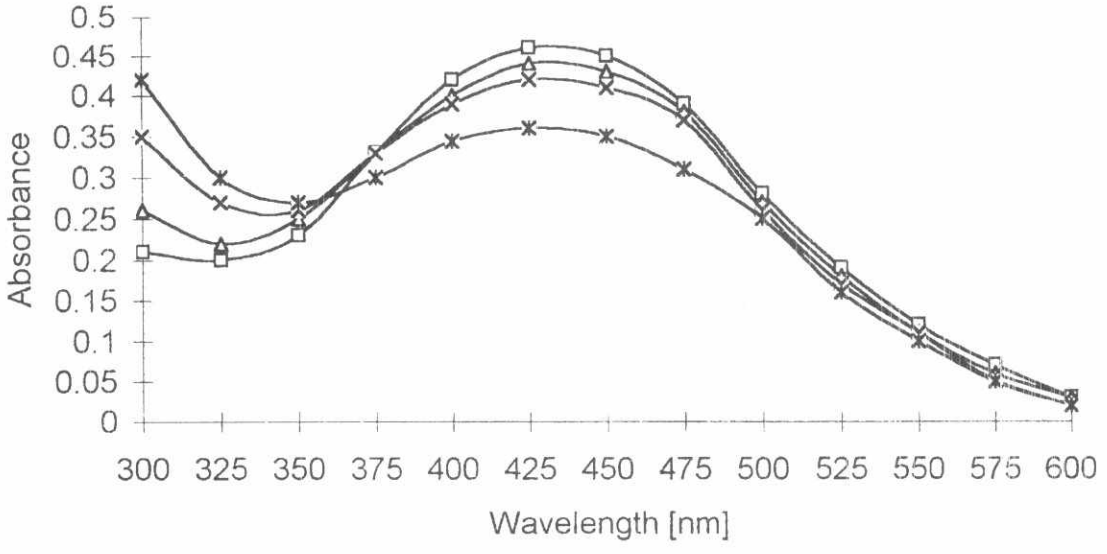

Fig. 6 Spectra of Fe(III)-D prepared at pH 5 under doses 200(□), 400(◊), 600(△), 800(×) and 1000(∗)Krad

Table 3 The absorbances at λ=426 nm and pH values for Fe(III)-D complexes prepared at pH 5 at concerned doses:

Dose (krad)	Absorbance A	A%	pH
-----	0.654	100	5
200	0.475	73	4.50
400	0.456	70	4.55
600	0.452	69	4.52
800	0.431	66	4.52
1000	0.372	57	4.65

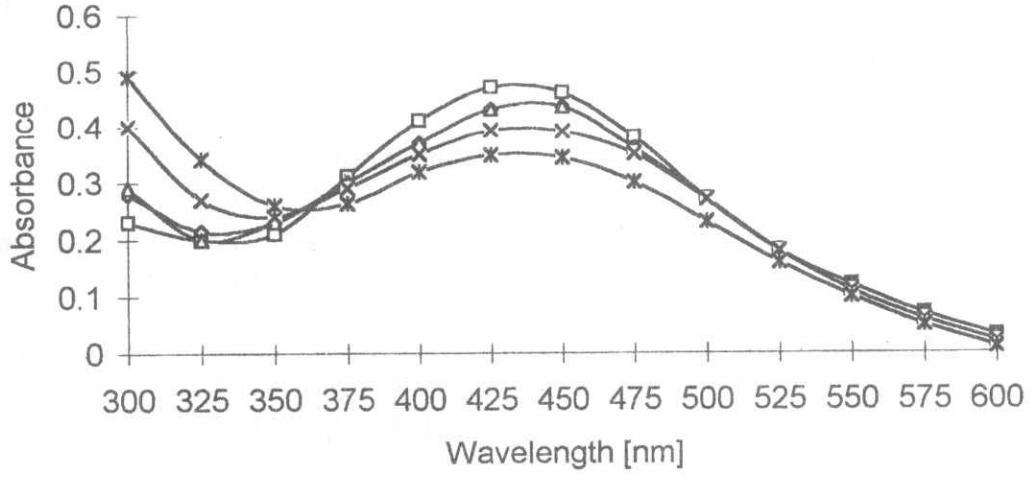

Fig. 7 Spectra of irradiated Fe(III)-D prepared at pH 5 under doses 200(□), 400(◊), 600(△), 800(×) and 1000(✳)Krad after 20 days.

Table 4 Effect of age on Absorbance and pH for Fe(III)-D prepared at pH 5:

Dose (krad)	After preparation		20 Days after preparation	
----	A	pH	A	pH
200	0.475	4.50	0.466	4.70
400	0.456	4.55	0.438	4.75
600	0.452	4.52	0.441	4.78
800	0.431	4.52	0.401	4.71
1000	0.375	4.65	0.354	4.78

Figure(8) demonstrates the spectra of irradiated Fe(III)-D through the doses under study at pH 7. From table(5),as absorbed dose increases the degradation increases but absorbance still with comparable percentage with respect to non irradiated samples. The irradiated sample by 1000 Krad gave absorbance of 62.5% of that of non-irradiated one. The pH values of the irradiated samples decreased approximately by 2.2. This means the liberation of acidic fragment due to radiolysis.

Here the difference in pH is clear due to the relative higher value of pH of preparation which is 7. Figure(9) demonstrates the spectra of samples for different doses after 20 days. Table(6) summarizes the effect of age on irradiated samples through absorbances and pH. From the table it appears that at each dose value the absorbance decreases except for dose of 200 Krad.

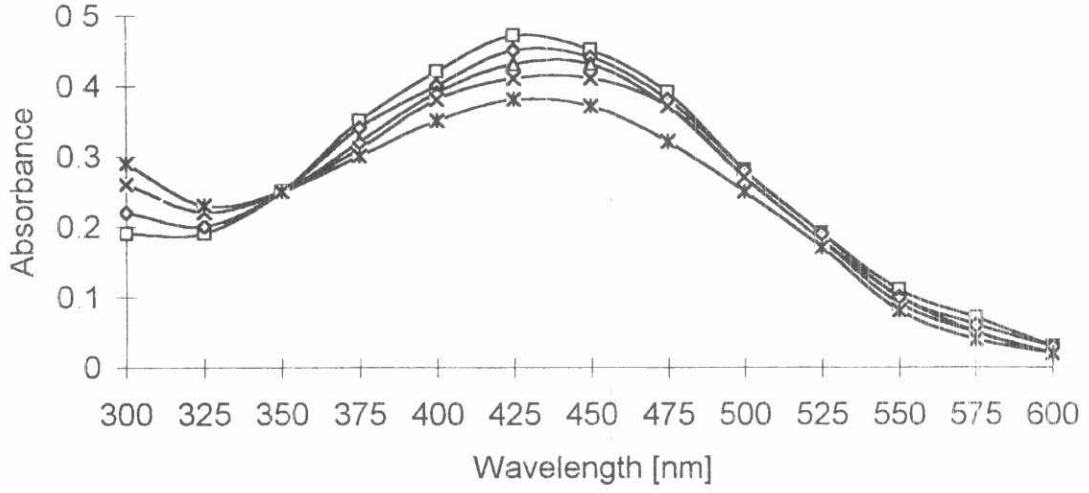

Fig. 8 Spectra of Fe(III)-D prepared at pH 7 under doses 200(□), 400(◊), 600(△), 800(×) and 1000(✳)Krad

Table 5 Absorbances at λ =426 nm and pH values for Fe(III)-D complexes prepared at pH 7 at concerned doses :

Dose (krad)	Absorbance	A%	pH
---	0.620	100	7.00
200	0.481	77.6	4.80
400	0.465	75.0	4.70
600	0.447	72.1	4.65
800	0.431	69.5	4.85
1000	0.389	62.7	4.50

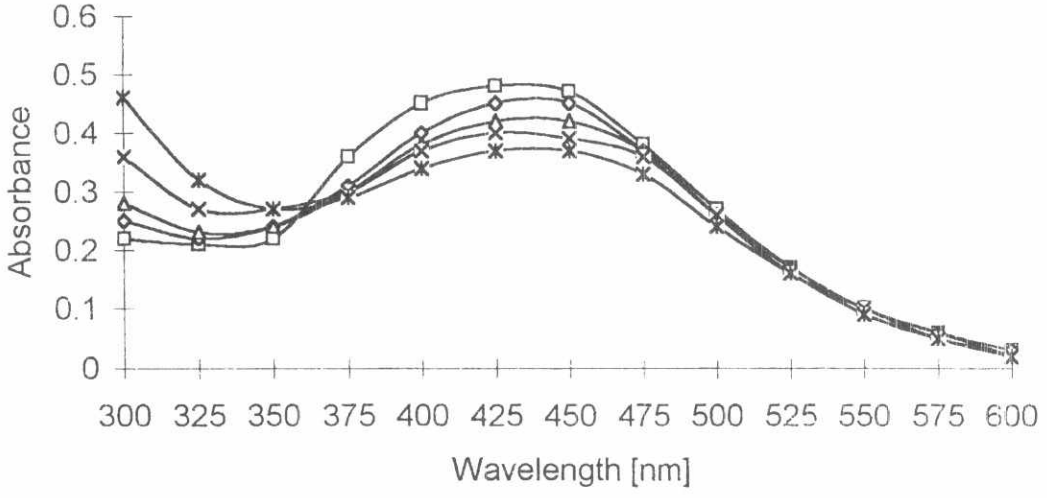

Fig .9 Spectra of irradiated Fe(III)-D prepared at pH 7 under doses 200(□), 400(◊), 600(△), 800(×) and 1000(✳) after 20 days.

Table 6 Effect of age on irradiated samples through absorbances and pH:.

Dose (krad)	After preparation		20 days After preparation	
	A	pH	A	pH
200	0.481	4.8	0.492	4.87
400	0.465	4.7	0.459	4.87
600	0.447	4.65	0.432	4.88
800	0.431	4.85	0.420	5
1000	0.389	4.5	0.379	5.12

Figure(10) displays the spectra of irradiated Fe(III)-D through the doses under study at pH 9. From table(7), it can be concluded that as dose increases the complex breaks down but still with comparable percentage with respect to non irradiated. The irradiated sample by 1000 Krad gave absorbance of 59.9% of that of non irradiated one. The pH values of the irradiated samples decreased approximately by 3.1 the same as in case of pH 7. Figure(11) shows the spectra of samples for different doses after 20 days. Table(8) summarizes the effect of age on irradiated samples through absorbances and pH. From the table it appears that at each dose value the absorbance decreases.

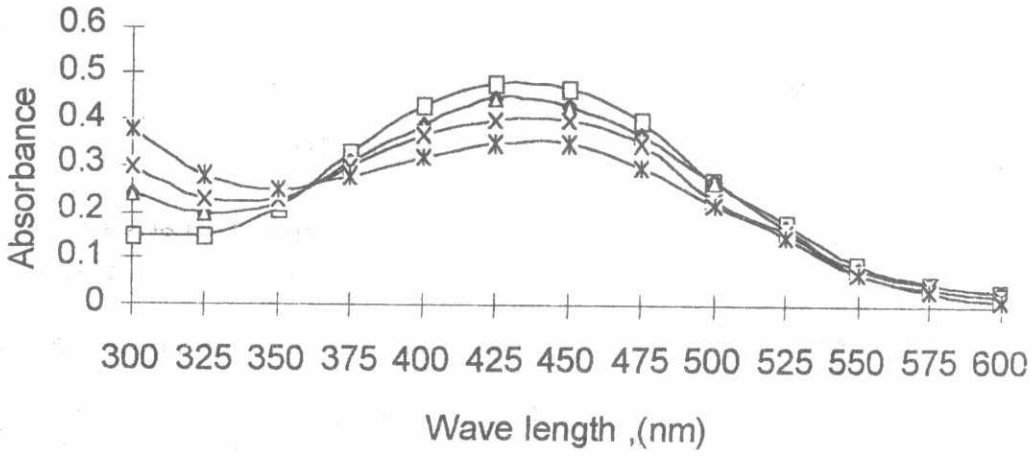

Fig. 10 Spectra of Fe(III)-D prepared at pH 9 under doses 200(□), 400(◊), 600(△), 800(×) and 1000(✱)Krad

Table 7 Absorbances at λ=426 nm and pH values for Fe(III)-D complexes prepared at pH 9 at concerned doses :

Dose (krad)	Absorbance	A%	pH
---	0.606	100	9
200	0.495	81.7	6
400	0.451	74.4	5.8
600	0.451	74.4	5.6
800	0.414	68.3	5.9
1000	0.363	59.9	5.6

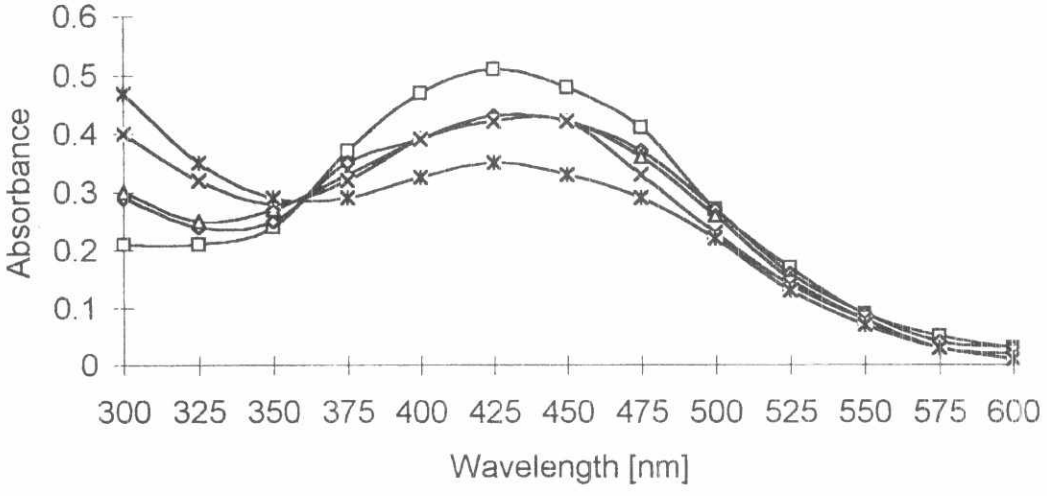

Fig. 11 Spectra of irradiated Fe(III)-D prepared at pH 9 under doses 200(□), 400(◇), 600(△), 800(×)and 1000(✳)Krad after 20 days.

Table 8 Effect of age on irradiated samples through absorbances and pH:

Dose (krad)	After preparation		20 days After preparation	
	A	pH	A	pH
200	0.495	6	0.505	6.6
400	0.451	5.8	0.432	5.8
600	0.451	5.6	0.440	5.6
800	0.414	5.9	0.422	6.4
1000	0.363	5.6	0.348	5.5

CONCLUSION

Desferrioxamine behaves as a good chelating agent for iron(III) forming 1:1 complex. The formed is stable at pH 5, 7 and 9. The degradation of the formed complex is due to radiolysis but the degradation is not so severe even for high-energy dose. Desferrioxamine is well known drug being used for certain therapeutic cases, so it is well examined with controlled side effects. Desferrioxamine can be considered as a radioactive-iron-decontaminating agent. Further examination of desferrioxamine as a chelating agent for different radioactive isotopes may point to its effectiveness and its use as a universal internal decontaminating agent against radioactive isotopes.

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