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STUDY OF DESFERRIOXAMINE-COPPER COMPLEX FORMATION

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ABSTRACT

Desferrioxamine-Copper complex was investigated. The effect of pH and the ratio of desferrioxamine to copper were studied .The apparent stability constants for complex formed at different pH values were determined .The effect of adding EDTA (desferrioxamine of 1%EDTA)on complex formation ratio and stability was studied .The results showed an increase in absorbance and stability in case of EDTA addition and the chelation ratio (metal:chelate) also changed from 1:1 to 2:1.

KEY WORDS

Desferrioxamine, Copper, Chelation, Drug, Internal decontamination.

INTRODUCTION

Heavy metal contamination of environment is common at many hazardous waste sites in many industrial zones. Lead , chromium , cadmium , copper , zinc , and mercury are most often observed metal contaminants .In numerous national sites , they have been found to be at elevated concentrations .

Activities contributing to heavy metal contamination of environment include vehicle emission , mining , smelting , metal plating/finishing , battery production , recycling , agricultural/industrial chemical applications , and incineration processes.

Heavy metals are toxic to people and pose a great risk for safe groundwater supply[1-3].Unbalancing bodies with such metal causes a number of diseases and removal of such toxic elements from bodies is of great importance[4].

This study investigates The formation of Desffereoxamine-copper complex by the continuous variation method .Copper decontamination using desferrioxamine and enhanced desferrioxamine as a drug is encouraging[5-6].

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MATERIALS AND METHODS

The salts used: Cu(II)chloride , desferrioxamine ,sodium hydroxide, hydrochloric acid were of analytical grade .Bidistilled water was used for preparation of stock solutions.

The samples of desferrioxamine-copper complex were prepared with different values of f, where $f=[Cu]/[Cu]+[D]$[3].[D] is the concentration of desferrioxamine and [Cu] is the concentration of copper such that $[Cu]+[D]=constant$ value .The value of f varies from 0.1 to 0.9.The samples were prepared from different volumes of solutions of desferrioxamine and copper of concentration 5×10^{-2} M such that the total volume of a sample was 5 ml .The pH of prepared samples and the reference samples were adjusted at 5,7 and 9 by the pH meter FISHER model 230A.

The optical measurements of the samples were carried out at laboratory temperature , of 25°C , by a shimadzu UV-Visible spectrophotometer UV-160.The samples of desferrioxamine and desferrioxamine-copper complex were evaporated gently under IR lamp till dryness then the IR spectra of the crystals obtained were recorded using ATI unicam FTIR.

RESULTS

Figure(1) demonstrates the spectra of Cu(II),desferrioxamine ,and desferrioxamine-copper complex (symbolized Cu-D) at pH 5 , 7 and 9. The peaks of Cu(II) and Cu-D are at 805 nm , 640 nm respectively with no peaks for desferrioxamine in the range of spectrum under study.

Figure(2) demonstrates the spectra of Cu-D complex for different values of f at pH 5,7 and 9.Results show that Cu-D was formed at $f=0.5$ for different pH values 5,7 and 9 with the maximum wave length λ at 640 nm .The absorbance values A at maximum wave length were plotted against the corresponding values of f in *figure (3)*.

From the curves the apparent stability constants $K^{'}$ of the complex formed with ratio M:D equals 1:1 (at f=0.5)at pH 5,7 and 9 were calculated using job's method as follows[7,8]:

$$Cu + D \rightleftharpoons CuD$$

$$K^{'}=\frac{[CuD]}{[Cu][D]}=\frac{\frac{A}{A^{'}}*C}{\left(\frac{A^{'}-A}{A^{'}}\right)*C*\left(\frac{A^{'}-A}{A^{'}}\right)*C}=\frac{\frac{A}{A^{'}}}{C*\left(1-\frac{A}{A^{'}}\right)^{2}}$$

where A is the actual absorbance of the complex, $A^{'}$ is the limiting absorbance if all ions were transferred completely to the complex form and C is the concentration of desferrioxamine at $f=0.5$.By substitution of values of A , $A^{'}$ and C ,the apparent stability constant values $K^{'}$ were calculated and found to be 1676 , 4201.4 , and 6964.7 for complex formed at pH 5 , 7 ,and 9 respectively.

Figure (4) demonstrates the UV spectra of (1%EDTA desferrioxamine)-copper complex (symbolized Cu-DE) for different values of f with the maximum wave length λ at 640 rim at pH 5,7 and 9.
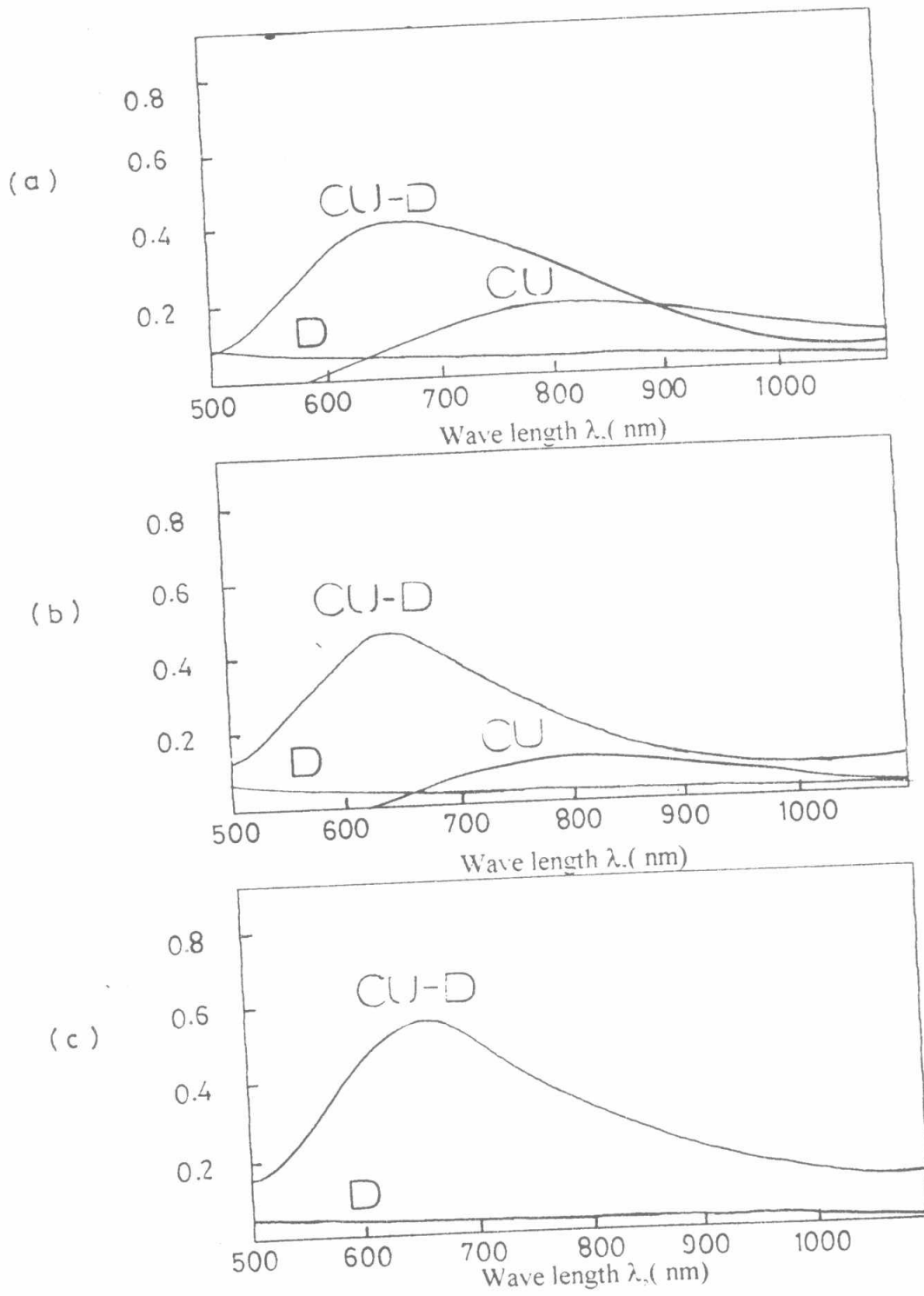
(a)

(b)

(c)

Fig.1. Spectra of Cu(II), Desf .Cu-D complex at pH 5(a),7(b), and 9(c).
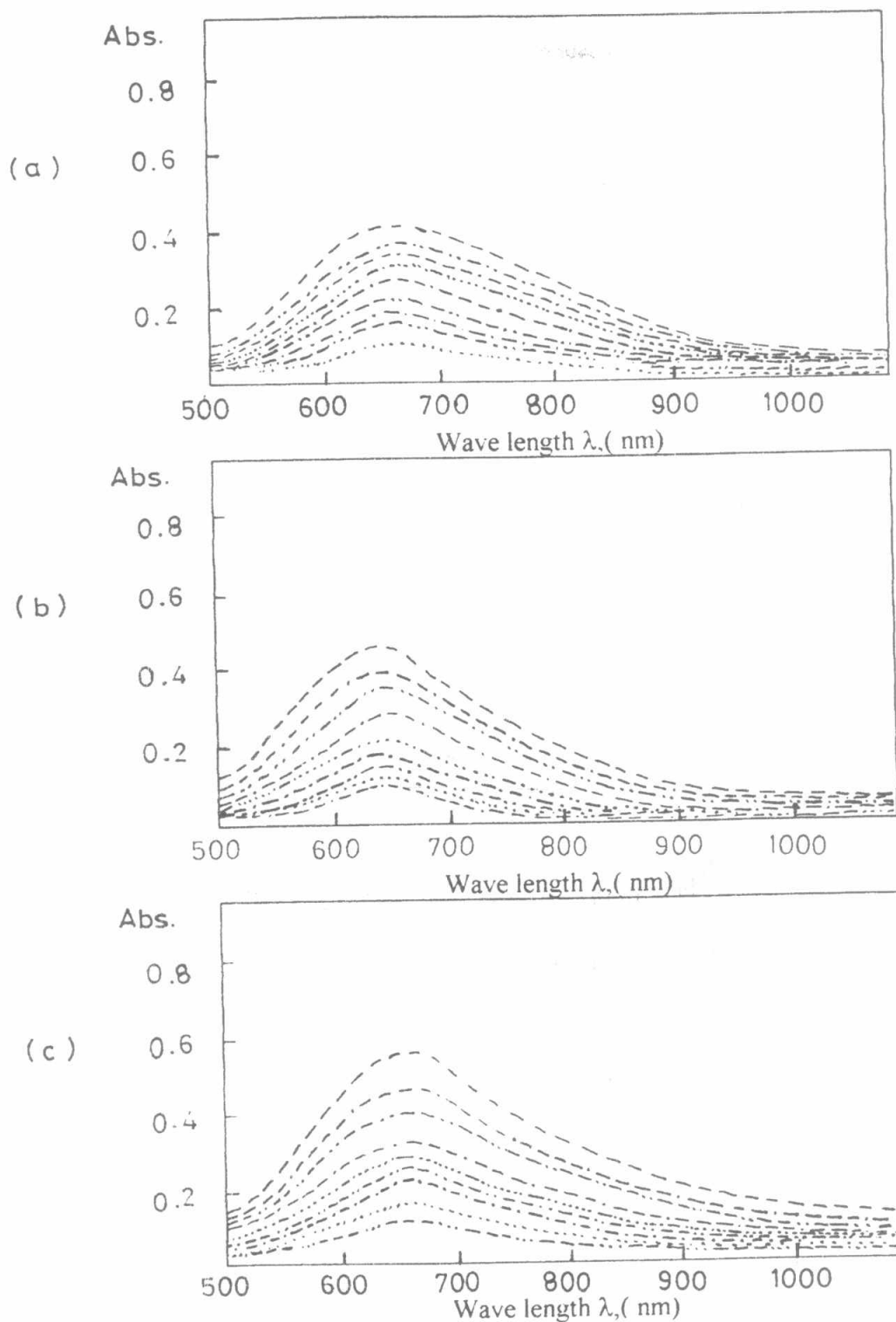
Fig.2. Absorption spectra of Cu-D complex for different values of f at pH 5 (a),pH 7 (b),and pH 9 (c) denoting for f=0.1,.../f=0.2,-.-/f=0.3,---/f=0.4,----/f=0.5,--- /f=0.6,-..-/f=0.7-.........-/f=0.8,--../f=0.9,---... .

Cu(II)D,pH=5,wl=640nm

(a)

Cu(II)D,pH=7,wl=640nm

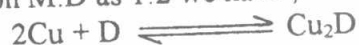(b)

Cu(II)D,pH=9,wl=640nm

(c)
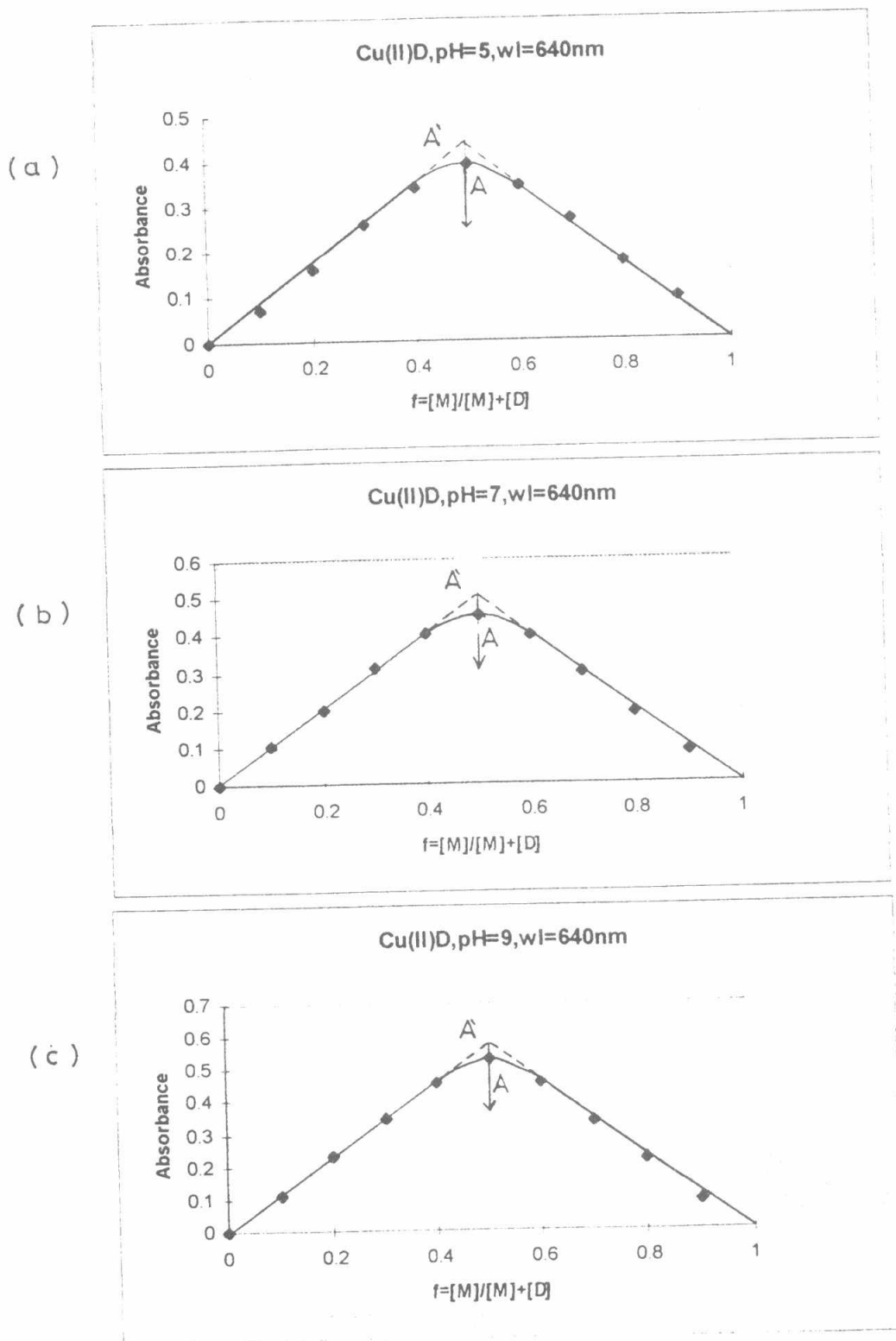
Fig.3. Variation of optical absorbance A with f at λ=640 nm for Cu-D at pH 5(a),7(b),and 9(c)

Figure (5) displays the absorbance values A at maximum wave length drawn against corresponding values of f. The results showed that complex Cu-DE was formed at $f = 0.66$ (M:D = 2:1).

$K`$ for Cu-DE can be determined as follows :

In case of complex formation M:D as 1:2 we have ;

$$2Cu + D \rightleftharpoons Cu_2D$$

$$\therefore K` = \frac{[Cu_2D]}{[Cu]^2[D]}$$

Let C is the concentration of desferrioxamine at equilibrium ;

$$K` = \frac{\frac{A}{A`} * C}{\left(\frac{\Delta A}{A`} * 2C\right)^2 \left(\frac{\Delta A}{A`} * C\right)} = \frac{\frac{A}{A`}}{\left(\frac{\Delta A}{A`}\right)^3 * 4C^2}$$

Where ΔA equals $A`-A$.

The apparent stability constants $K`$ were calculated and found to be 1.188×10^5 , 3.527×10^4 , and 1.133×10^5 for the complex formed at pH 5 , 7 , and 9 respectively . Therefore it can be concluded clearly from results that addition of small amount of EDTA (1%) cause high reactivity of desferrioxamine for complexation since it changed the ratio of M:D from 1:1 to 2:1 and produced more stable complexes with higher $K`$ than without addition of EDTA .

Figure (6) shows the IR spectra of desferrioxamine at pH 5,7,and 9. The comparison shows that the structure of desferrioxamine changes as pH value changes ,and this is due to the presence of amino groups which are sensitive to pH value.

Figure (7) demonstrates the IR spectra of Cu-D complex at the same pH values 5 ,7 ,and 9. From *figures (6,7)* it is clear that the structure of not chelated desferrioxamine differs from that in the complex form at each value of mentioned pH with slight difference at pH 9. This structure difference is only due to formation of complex.
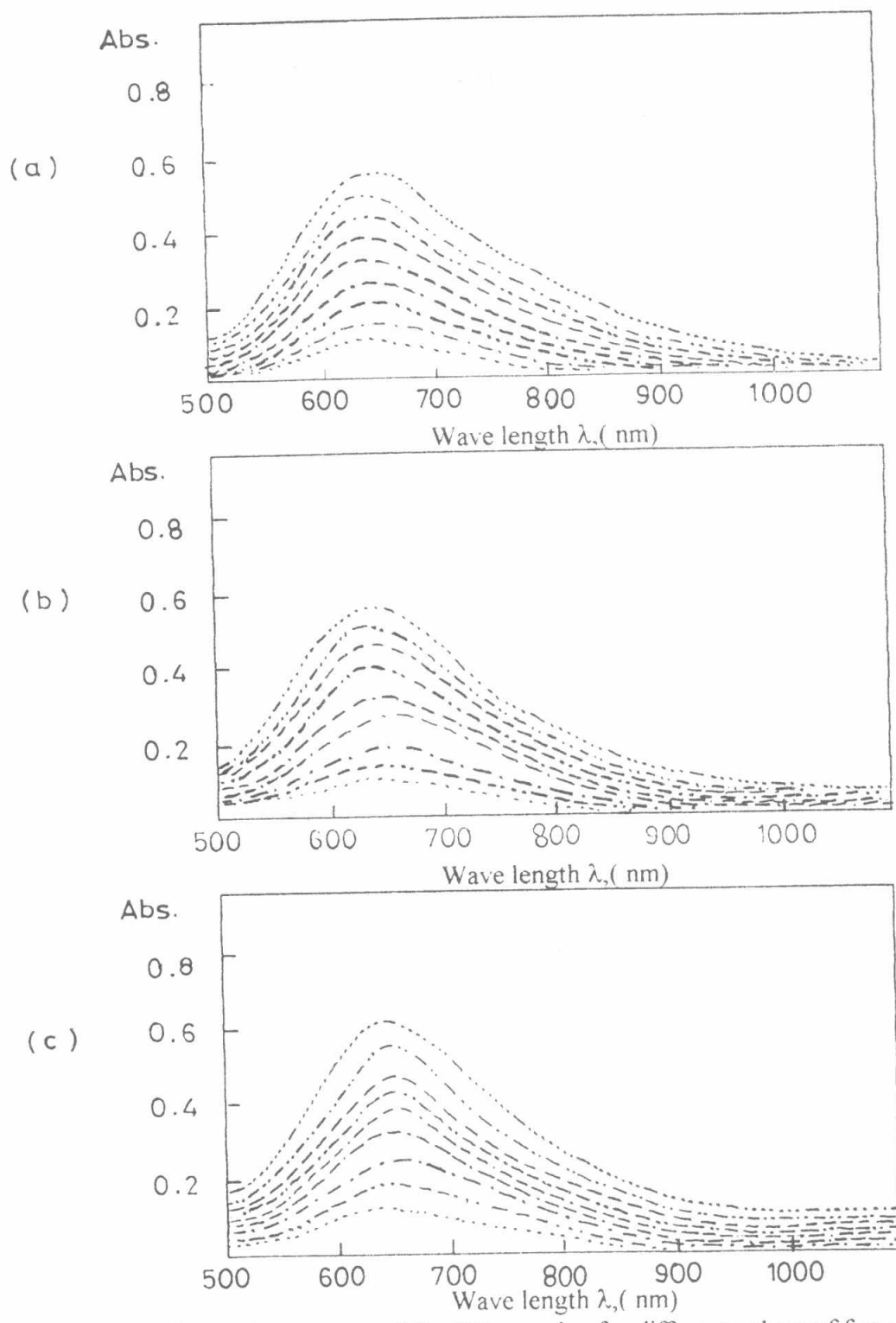
Fig.4. Absorption spectra of Cu-DE complex for different values of f at pH 5 (a),pH 7 (b),and pH 9 (c) denoting for f=0.1,.../f=0.2,-.-/f=0.3, ---./f=0.4,-----/f=0.5,--- /f=0.6,-..-/f=0.7-........-/f=0.8,--../f=0.9,---...

Cu(II)DE,pH=5,wl=640nm

(a)

Cu(II)DE,pH=7,wl=640nm

(b)

Cu(II)DE,pH=9,wl=640nm

(c)

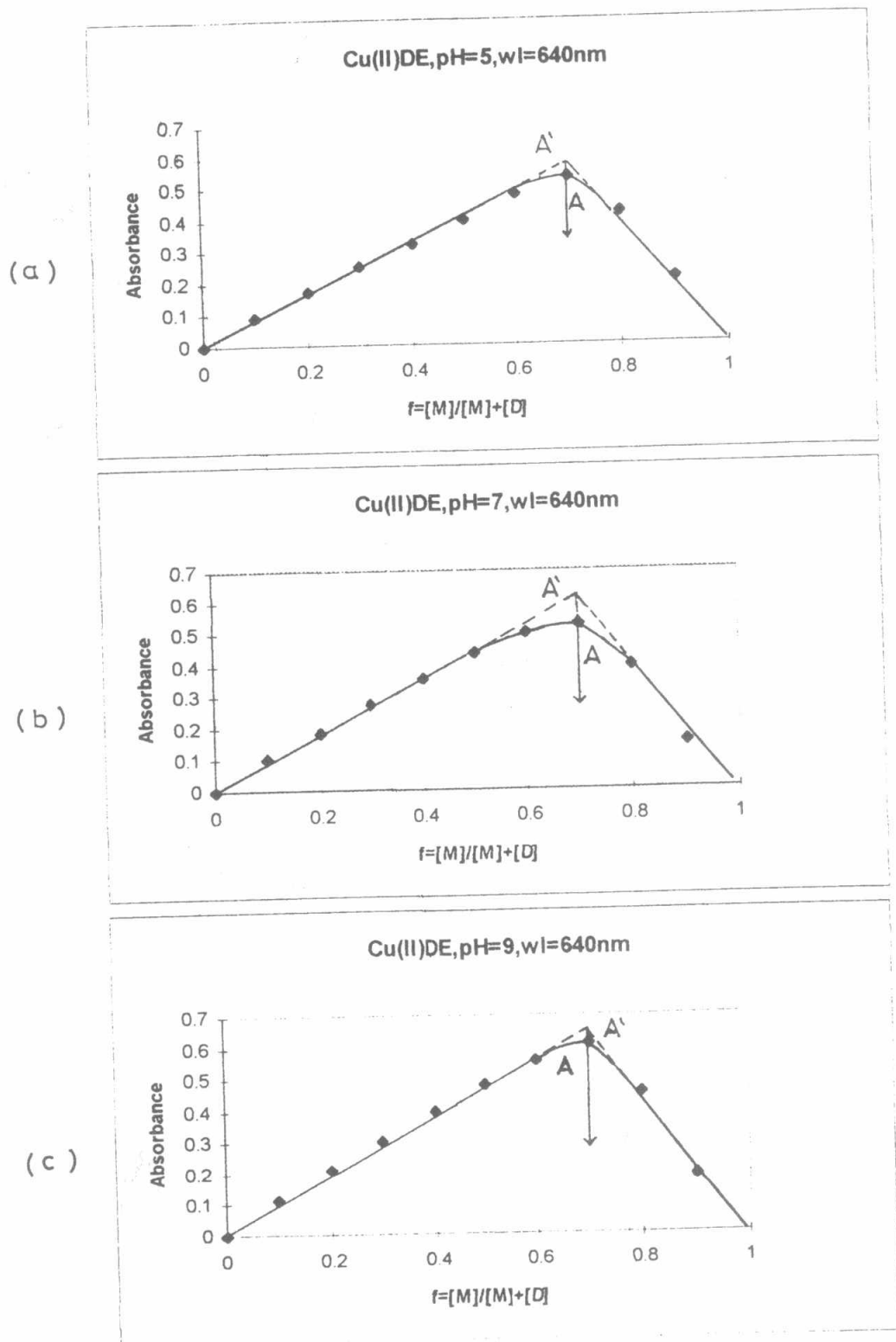**Fig. 5.** Variation of optical absorbance *A* with *f* at λ=640 nm for Cu-DE at pH 5(a),7(b),and 9(c)
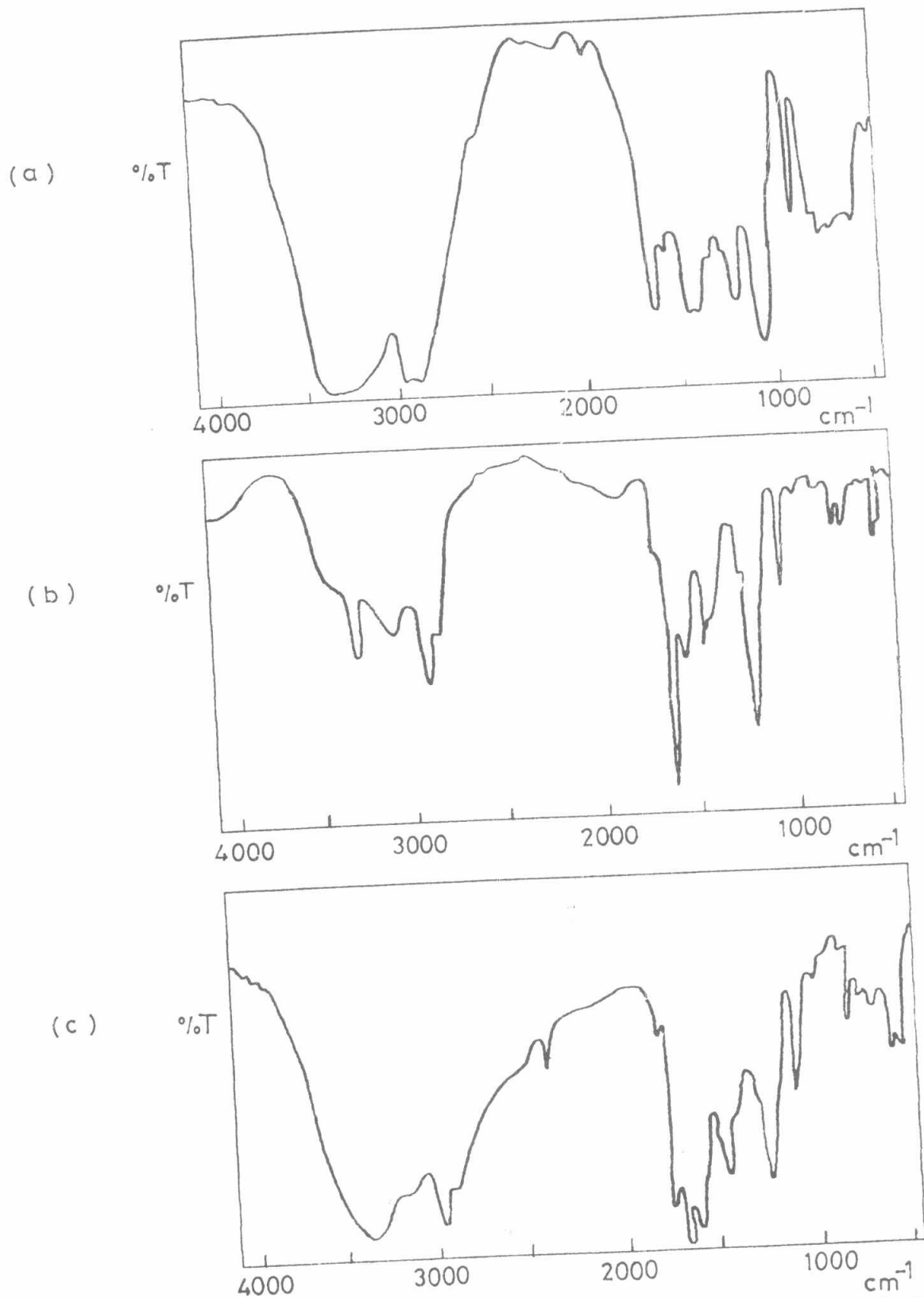
Fig. 6. IR spectra of desferrioxamine at pH 5 (a), pH 7 (b),and pH 9 (c).
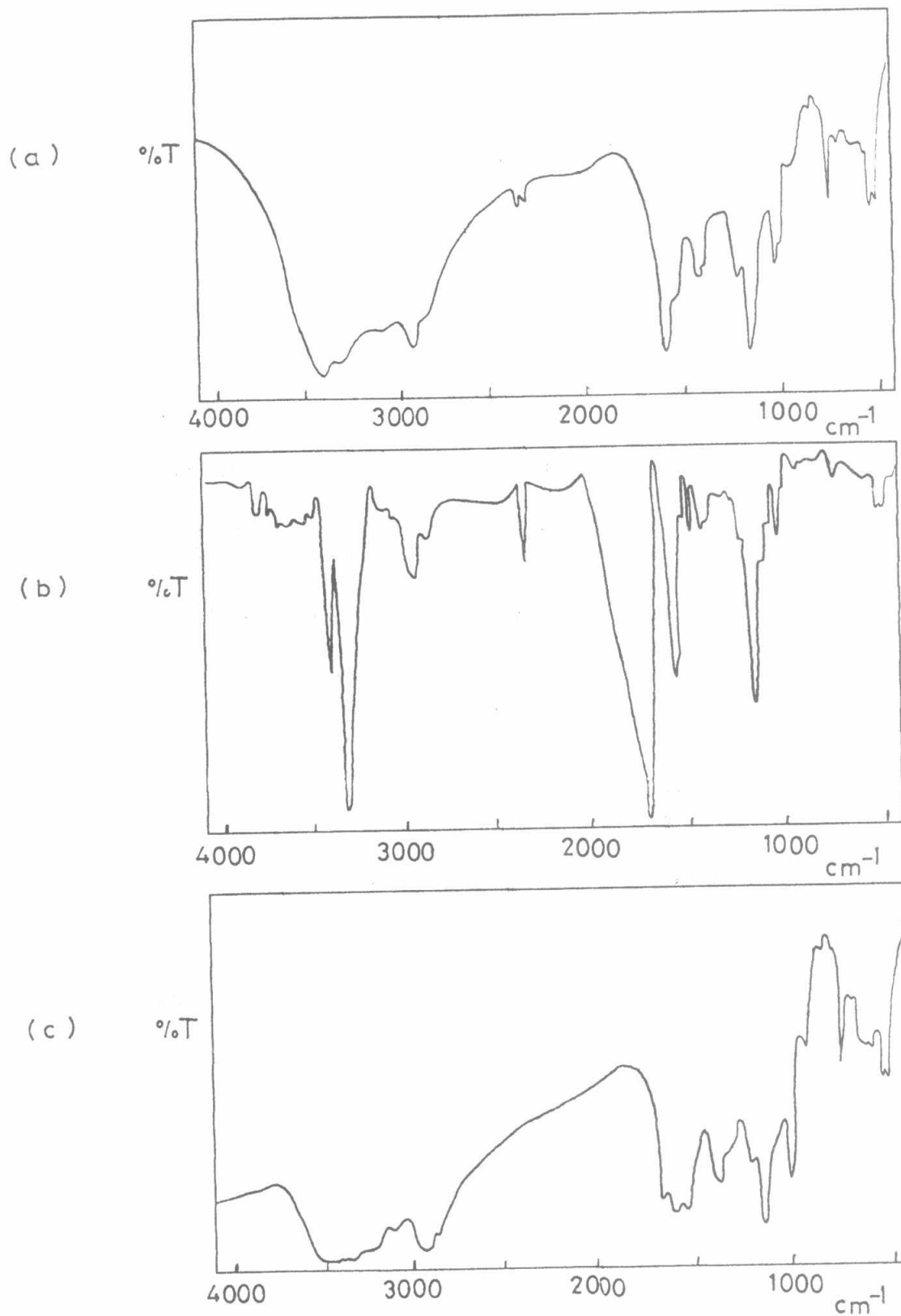
Fig. 7. IR spectra of Cu-D complex at pH 5 (a), pH 7 (b), and pH 9 (c).

CONCLUSION

Desferrioxamine shows good affinity towards copper and stable Cu-D complexes for studied range of pH are formed. The addition of EDTA by only 1% to desferrioxamine decreased the amount of desferrioxamine needed to chelate the same amount of copper to one half and thus the side effects of its administration are minimized.

This result is very important for practical use of desferrioxamine as an effective chelating drug for internal decontamination of human body in case of excess copper toxicity or excess radioactive copper.

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