International Journal of PharmTech Research
CODEN (USA): IJPRIF, ISSN: 0974-4304, ISSN(Online): 2455-9563
Vol.9, No.5, pp 292-298, 2016

Spectrophotometric Study of complex formation between Hematoxylin and Al^{3+} and Fe^{3+} ions

Angham G. Hadi*, Eman H. Humedy, Nahla S. Saddam, Ferdoos S. Abd-alameer[1]

Chemistry Department, College of Science, Babylon University/ Hilla-Iraq,

Abstract : In this research work deeply blue and black complexes are formed from Hematoxylin with Al^{3+} and Fe^{3+} ions respectively. The optimum conditions of (concentration, volume, pH and temperature) and The UV-Visible spectra of these ions with pigment solution have been analyzed.
The formula of complexes is deduced according to the Molar ratio method which is gained from the spectrophotometric studies of the complex solution. The ratios of ligand: metal obtained were 3: 1 for two complexes under study.
The solid complexes are indicated by UV- Visible spectra that showed red shift when it compared with pigment solution spectra. Additionaly infrared spectra are analyzed and showed appearance and disappearance of some peaks. This refers to coordination between ligand and metal ions.
Keywords : Hematoxylin, metal ions, coordination, complex.

1 Introduction

Hematoxylin is a natural dye extracted from the wood of the Logwood tree found in Mexico and Central America. [1].Haematoxylon is put from Greek, haimatodec (blood-like) and xylon (wood) Fig.1. Hematoxylin by itself cannot stain. It requires to oxidize to hematein, which process is considered as ripening. Ripening can proceed spontaneously and tardily by exposure to atmospheric oxygen, or speedly by added chemical oxidants such as mercuric oxide (Harris) or sodium iodate (Gill).

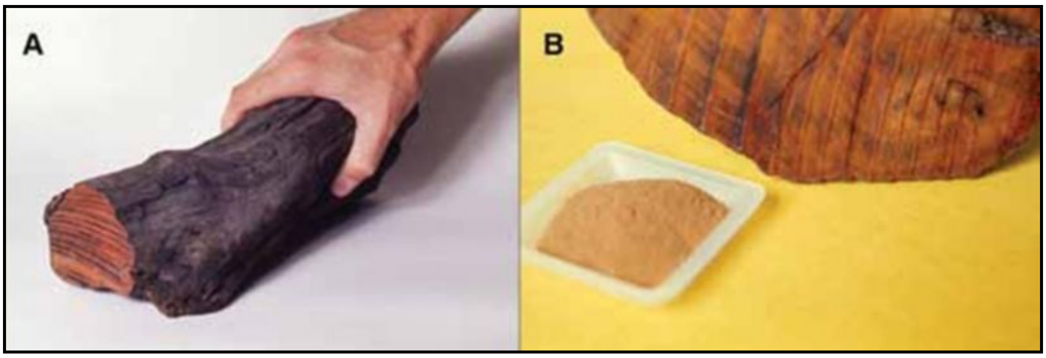


Figure 1. (A) Logwood, (B) cut end of same logwood and hematoxylin powder

Hematoxylin powder or crystals already contain hematein. Numerous oxidants have been used historically, but sodium iodate is adopted because it oxidizes at room temperature and is environmentally friendly (and does not contain mercury).

Using half the sodium oxide deserved to oxidize the entire amount of hematoxylin is intended to ensure that it is not overoxidized initially, which would produce a product with a short useful shelf-life. Figure 3 shows the stoichiometric oxidation of one gram of anhydrous hematoxylin by 217.7 mg sodium iodate. Nominally half that amount, 100 mg, is used to halfoxidize hematoxylin. Also, staying hematoxylin can continue to be spontaneously oxidized slowly by atmospheric oxygen to save the strength of the solution.

Aluminum sulfate$Al_2(SO_4)_3$ is a chemical compound that's applied to as sulfuric acid, aluminum salt, or cake alum. It has many applications, including waste treatment, water purification, and paper manufacturing.

It is a white or off-white crystalline solid or powder. The compound is made by sum aluminum hydroxide to sulfuric acid. It's hygroscopic, that means it has the ability to absorb and hold water molecules from the surrounding atmosphere. It's correspondingly water soluble and not volatile or flammable.

It is water soluble and is utilized as a flocculating agent in the purification of drinking water [2,3]

Aluminium sulfate is used in water purification and in dyeing and printing. In water purification, it makes impurities to coagulate into bigger particles and then settle to the bottom of the container more easily. This process is called coagulation or flocculation. [4]

In industrial application, iron (III) chloride is utilised in drinking water production and sewage treatment .[5]Another important application of iron(III) chloride is impression copper in two-step redox reaction to copper(I) chloride and then to copper(II) chloride in the production of printed circuit boards.[6]Reacts with cyclopentadienylmagnesium bromide in one development of ferrocene, a metal-sandwich complex.[7]

Alsoitsusedin conjunction with NaI in acetonitrile to lower organic azides to primary amines.[8]Used in an animal thrombosis model.[9]

2. Materials and Methods

2.1 Hematoxylin oxidizing

0.0033 Molesofhematein is prepared by adding 1gm of hematoxylin to 0.0011 moles sodium Iodate solution ($NaIO_3$) as in figure2.

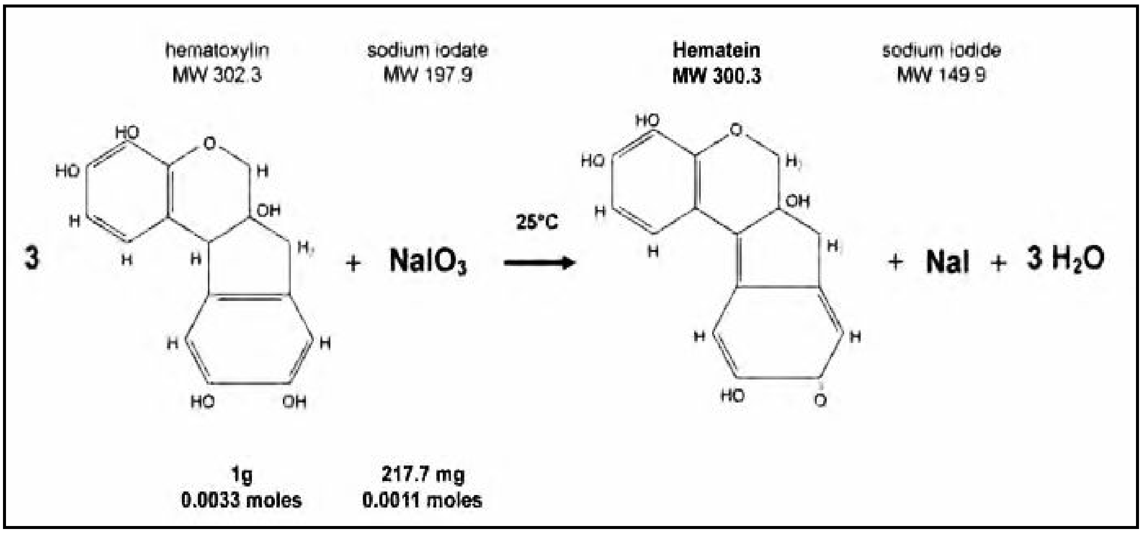


Figure 2. Stoichiometric oxidation of hematoxylin.

2-2 Salts Preparation

0.0033 moles of Al (III) and Fe (III) was prepared by dissolving and gm respectively in distilled water The pH was adjusted by using dilute solutions from HCl and NaOH in the range of (1-8).

2-3 Molar-Ratio Method

The experiment was achieved according to the method described by Jines and Yoe [10], 1 ml of 0.0033 M Al (III) was added to series 10ml flasks contain (0.5,1, ...4) ml of 0.0033 M solution of the hematein, the mixtures were kept at pH 3.0 and the volume was completed to the mark with distilled water the absorbencies were recorded at 586 nm. The experiment was repeated for Fe (III).

3. Results and Discussion

3-1 Identification of the hematoxylin and the Complexes

Major information can be acquired from the spectral characteristics of hematoxylin. Two distinctive absorption bands one in the UV-region (270 to 283 nm) and the second in the visible region (400 - 500nm). The absorption spectrum of hematoxylinwas shown in Figure3.

Addition of $Al_2(SO_4)_3$ and $FeCl_3$ to the solution of hematein resulted in a spectra shift as shown in Table (1). The spectra shift was as a result of the formation of coordination complex between hematein and the individual metal ions. A hematein -Al (III) complex was formed at pH 3.0 (λ_{max} = 586 nm); ahematein -Fe (III) complex was formed at pH 4.0(λ_{max} =492 nm), as shown in Figure 4 and 5.

Table (1):- represents the λ_{max} of hematein and complexes.

λ_{max} /nmof complexes	λ_{max} /nm of hematein
Al (III) 586	450
Fe (III) 592	

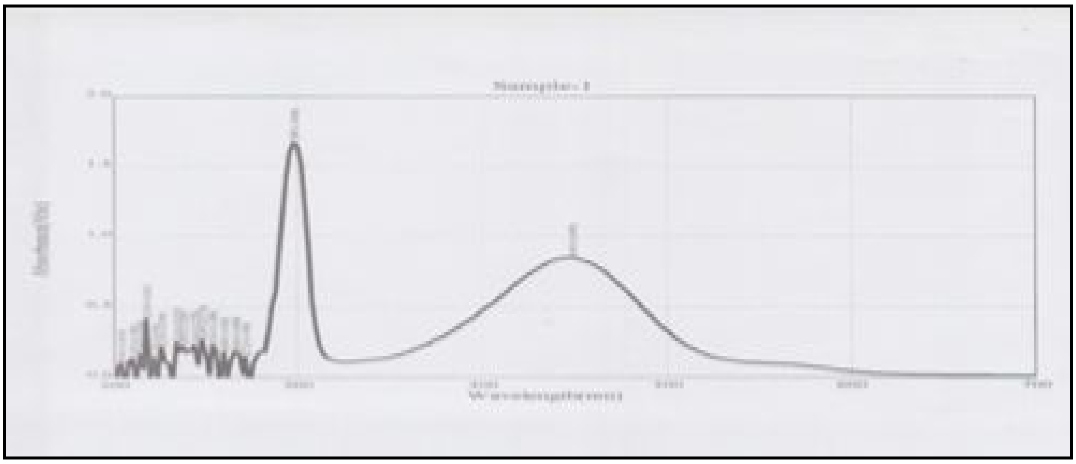


Figure 3.The absorption spectrum of hematoxylin.

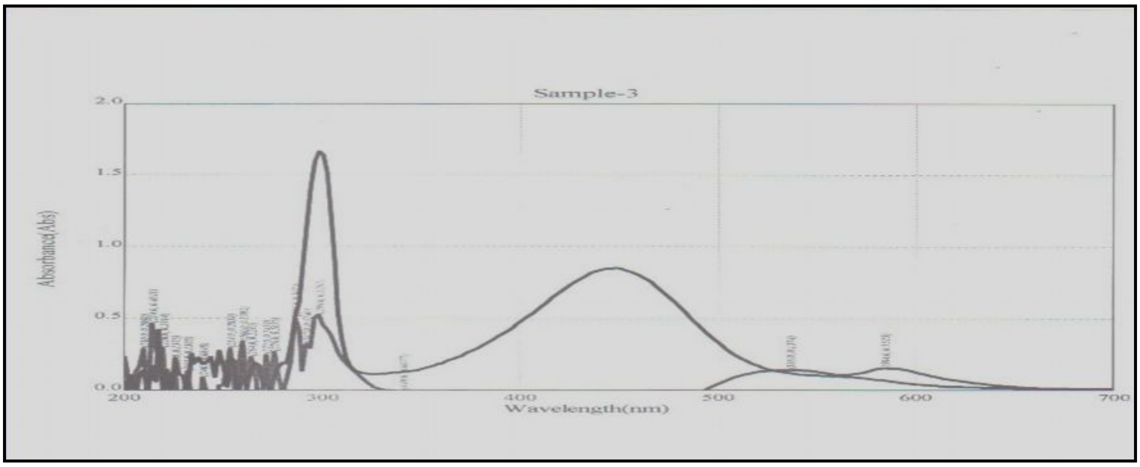


Figure 4.The absorption spectrum of hematoxylin-Alum complex.

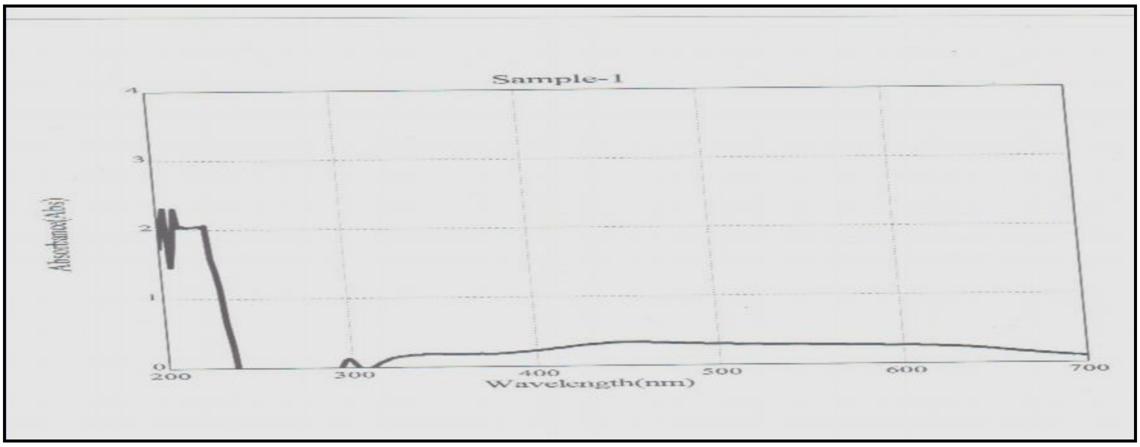


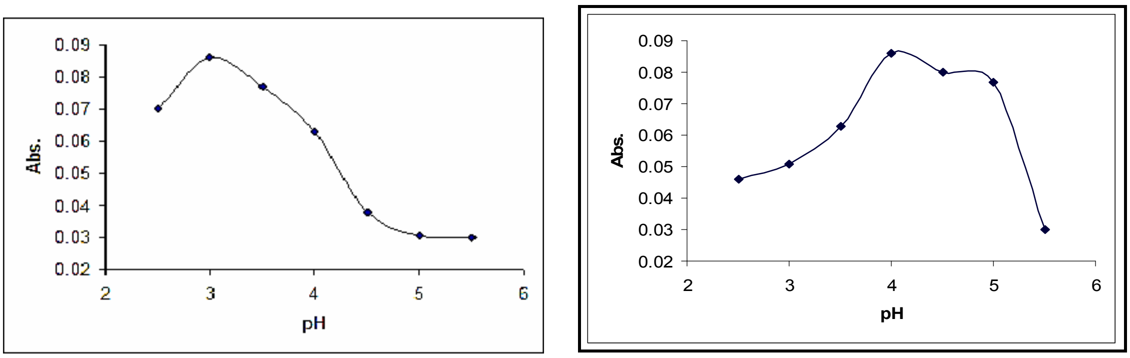
Figure 5.The absorption spectrum of hematoxylin-Ferric complex.

3-2 pH Effect

The pH values of the mixing solutions of metals ions with hematein were very important in coordination process. This importance comes from deprotonation or stabilizing protons on active groups in ligand molecule. Every metal ion prefers certain pH when it's coordinate with ligand.

The optimum pH for complexes ion were 3.0 and 4.0 for Al (III) and Fe (III) respectively.

Figs. 6 and 7show the relationship between pH and absorbance of Al (III) and Fe (III) complexes.



Figures. 6 and 7 show the relationship between pH and absorbance of Al (III) and Fe (III) complexes.

3-3 Determination of metal: ligand Ratio in a Complex

3-3-1 Molar - Ratio Method

Solutions were prepared by fixing metal concentration and variation hematein concentration. The absorbances were measured at λ_{max} for each complex, the relationship between L: M and Absorbance was 3:1 as in Figure 8.

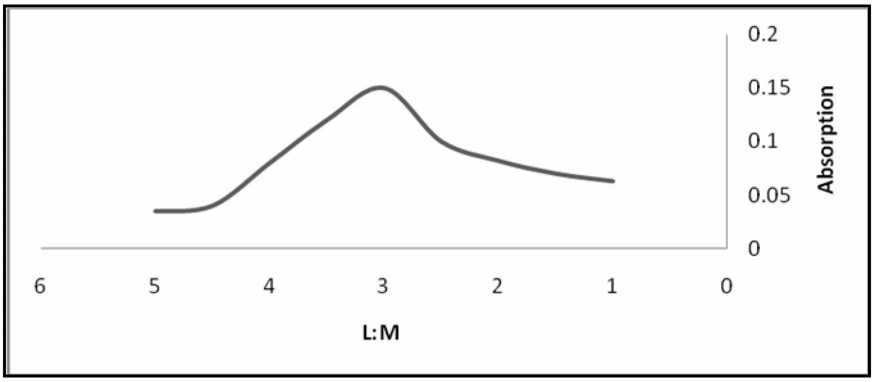


Figure. 8 relationship between L: M and Absorbance.

3-4 FTIR SPECTRA

Infrared absorption spectra[11-18] were obtained from (400 – 4000) cm⁻¹ using KBr tablets. Figures 9, 10and 11

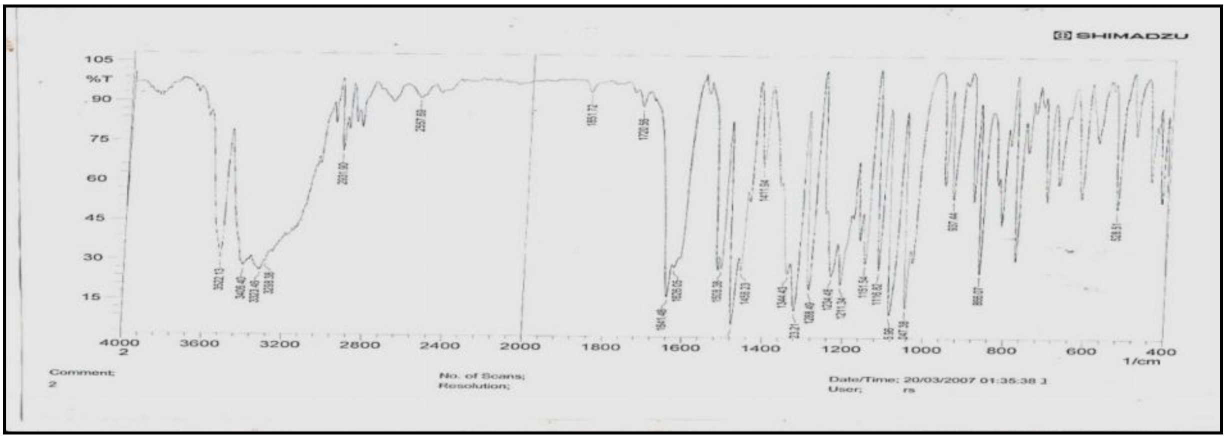


Figure9.Infrared absorption spectra of hematoxylin.

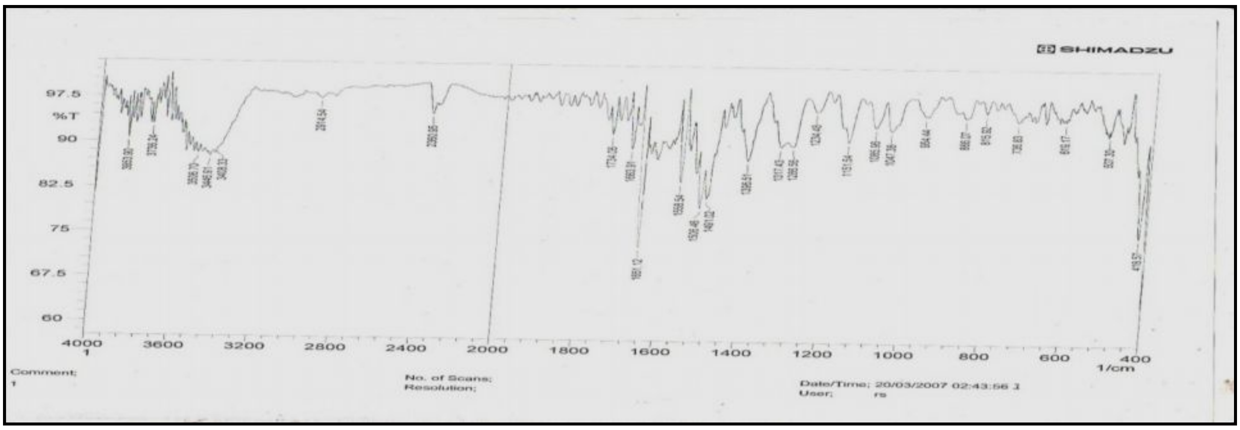


Figure 10. Infrared absorption spectra of hematoxylin--Alum complex.

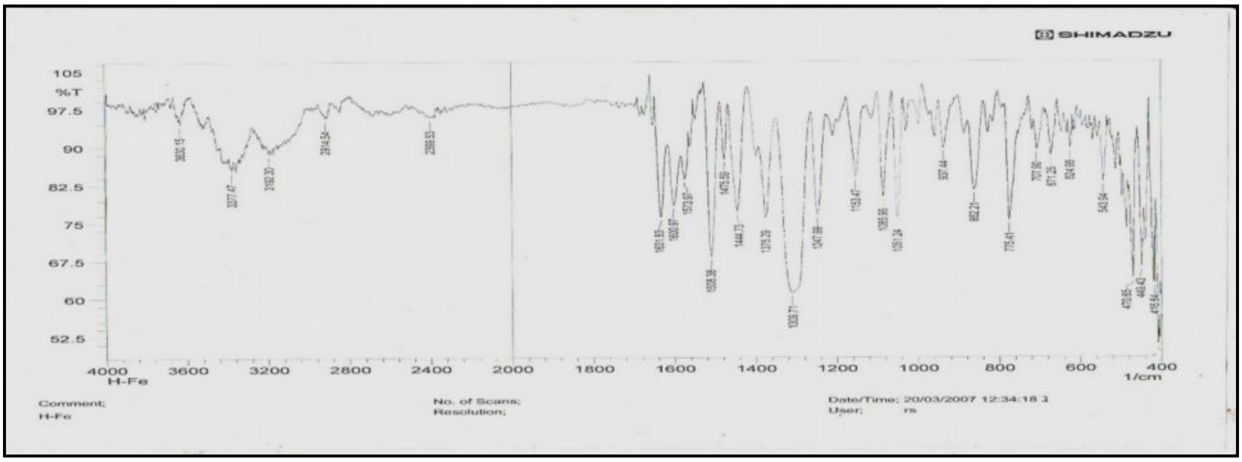


Figure 11. Infrared absorption spectra of hematoxylin--Ferric complex.

3-5 The Proposed Structural Formula of Complexes

In this study the oxidizing hematoxylin is bidentate, the attachment positions with metals ions Al (III) and Fe(III))were oxygen of hydroxyl group.According to the results and measurements that it can propose the structural formula of complexes that have a ratio of ligand: metal equal 3: 1 and the suggested figures are octahedral[19], as in Figure 12

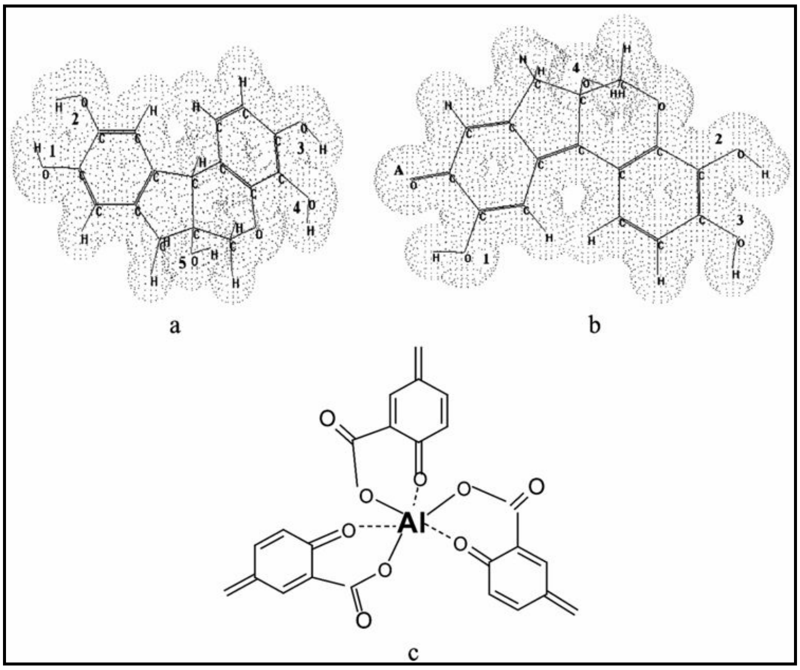


Figure 12.The expected structure of hematein-Alum complex.

References

1. Brown, G. G. (1978). An Introduction to Histotechnology. Appleton-Century-Crofts, New York.
2. Jump up^ Global Health and Education Foundation (2007). "Conventional Coagulation-Flocculation-Sedimentation". Safe Drinking Water is Essential. National Academy of Sciences. Retrieved 2007-12-01.
3. Kvech S, Edwards M (2002). "Solubility controls on aluminum in drinking water at relatively low and high pH". WATER RESEARCH36 (17): 4356–4368.
4. IljePikaar, Keshab R. Sharma, Shihu Hu, Wolfgang Gernjak, Jürg Keller, Zhiguo Yuan.(2014) "Reducing sewer corrosion through integrated urban water management". Retrieved 08-25.

5. Jump up Water Treatment Chemicals (PDF). Akzo Nobel Base Chemicals.(2007). Retrieved 10-26.
6. Jump up Greenwood, N. N.; A. Earnshaw (1997). Chemistry of the Elements (2nd ed.). Oxford: Butterworth-Heinemann.
7. Kealy, T. J.; Pauson, P. L. (1951). "A New Type of Organo-Iron Compound". Nature 168 (4285):
8. Kamal, Ahmed; Ramana, K.; Ankati, H.; Ramana, A (2002). "Mild and efficient reduction of azides to amines: synthesis of fused [2,1-b]quinazolines". Tetrahedron Letters 43 (38): 6961.
9. Tseng, Michael; Dozier, A.; Haribabu, B.; Graham, U. M. (2006). "Transendothelial migration of ferric ion in FeCl3 injured murine common carotid artery". Thrombosis Research 118 (2): 275–280.
10. Yoe, J. H. and Jones, A. L)1944 (; Ind. Eng. "Chem. Anal.", 16: 11,.
11. Jabbar, A.Z., , Hadi, A. G., and Sami, F.,. Oriental Journal of Chemistry, 2014. 30(2): p. 571-575.
12. Aljeboree A. M., Alshirifi A. N., and Alkaim A. F.,. Arabian J. Chem., 2014. 10.1016/j.arabjc.2014.01.020.
13. Jasim, F.A., , Lafta, F., Hashim, A., Ali, M., and Hadi, A. G.,. Journal of Engineering and Applied Sciences, 2013. 8(5): p. 140-142.
14. Hadi, A.G.,. British journal of science, 2012. 5: p. 33-38.
15. Aljeboree, A.M., A.F. Alkaim, and A.H. Al-Dujaili, Desalination and Water Treatment, 2015. 53(13): p. 3656-3667.
16. Hadi, A.G., British journal of science, 2012. 6: p. 2-7.
17. Karam F. F., Kadhim M. I., and Alkaim A. F. ,. Int. J. Chem. Sci., 2015. 13(2): p. 650-660.
18. Alqaragully, M.B., AL-Gubury, H. Y., Aljeboree, A. M., Karam, F. F., and Alkaim, A. F.,. Research Journal of Pharmaceutical, Biological and Chemical Sciences, 2015. 6(5): p. 1287-1296.
19. Hikmat; Y.R. (1999)Ph.D.Thesis, University of Mousl.

*****