Synthesis and Physico-chemical Studies of Some Heavy Metals Complexes with New Organic Ligand 4-((4-Formyl-2-Hydroxy Phenyl) Diazenyl)-N-(5-Methyl Isoxazol-3-yl) Benzene Sulfonamide

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Abstract
New complexes were synthesized with the following metals [Cu (II), Pb (II), and Hg (II] based on the new ligand of 4-((4-Formyl-2-Hydroxy phenyl) Diazenyl -N- (5-Methyl Isoxazol-3-yl) Benzene Sulfonamide (FDS). This ligand was synthesized via reaction of 4-amin-N- (5-methyl-1, 2-oxazol-3-yl) with (Para-hydroxy benzaldehyde) in the presence of alcohol alkaline solution. The prepared ligand and its chelating complexes have been diagnosed by different spectroscopic techniques such as ^{1}HNMR. The physical properties of the prepared compounds were evaluated. Based on Lambert-Beers law, the resulting ideal concentration ranged between 0.00001- 0.0001 M. To determine the stoichiometry of complexes, spectral studies were conducted for all of them, yielding a molar ratio of 1:2. The ligand has a bidentate behavior, and the final structures of complexes are hypothesized to be octahedral.
Keyword: Isoxazole, Metal complexes, Ligand, Coordination, Azo dye, Stoichiometry.

Introduction

Peter Greiss [1], discovered azo dyes in 1860, which is one of the largest versatile class in comparison with other types of dyes. It is notable by the presence of functional group; (-N=N-) symmetrical and/or asymmetrical alkyl or aryl radicals are correlated with at least one heterogeneous aromatic system. Many fields have the use of azo compounds including medicine [2], industry [3], agriculture [4] and analytical chemistry [5]. It also has a unique attention within the fields of biological activities [6], anticancer [7], pesticidal activities [8] plastics [9] and textile dyeing and leather [10]. The chemical composition of an azo dye consists of a backbone
(-N=N-), chromophoric, auxochrome, which are part of azo group in addition to soluble groups. The color of the azo dyes depends on the chromophores and auxochromes [11]. The determination of the metal ions is subjected to heterocyclic azo ligand with classification of stability and the interaction speed with ion metals and being categorized as highly sensitive chromogenic ligand thus resulting in large applications of spectrophotometric techniques due to these reactions [12][13]. 70% of the dyes used within the manufacturing sector are azo dyes [14]. Azo dyes that are used in the textile industries may be poisonous thus have a negative impact on the environment and public health [15], thus the waste water discarded by the textile industries must be treated accordingly [16]. Many physic-chemical techniques are used to treat wastewater discarded by fabric manufacturers [17]. Bacteria are utilized as an example of biological (aerobic and anaerobic) mechanisms that causes dye degradation [18].

Material and Methods

Chemicals and Reagents

Samarra Drug Industries, Merck, BDH and Fluka are the main suppliers for the chemicals used.
Pure sample of sulfamethoxazole, molecular formula $C_{10}H_{11}N_3O_3S$ and molecular weight (253.28)

Instrumentation

The Bruker processes are utilized for the analysis of the ^{1}HNMR spectra through the use of spectrophotometer (400 MHz) which includes the DMSO-d6 solvent for measuring purposes with TMS as an internal standardized reference. The metal ratio within the complexes can be determined through using UV-Visible spectrophotometer Shimadzu AA-7000 style flame atomic absorption system. A platinum electrode system; thermal and melting point system form (9300 u.k), Utilizing Cond.720 (WTW) is used to calculate the molar conductivity of the solution.
Synthesis of 4- ((4-Formyl-2-Hydroxyphenyl) Diazenyl)-N-
(5-Methyl Isoxazol-3-yl) Benzene Sulfonamide (FDS).
ligand is prepared through the use of shibata's method [19] with numerous adjustments on the diazotization linking reaction (Scheme.1). Equimolar (0.005) solutions of sulfamethoxazole (1.2664 g) with Para-hydroxy benzaldehyde (0.610613 g), were dissolved in absolute ethanol mixture (1:1).
The mixed solution will be cooled to (0°C) and $NaNO_2$ solution (0.345g) of sodium nitrite (10%) will be added, stirred continuous for (30 min) at

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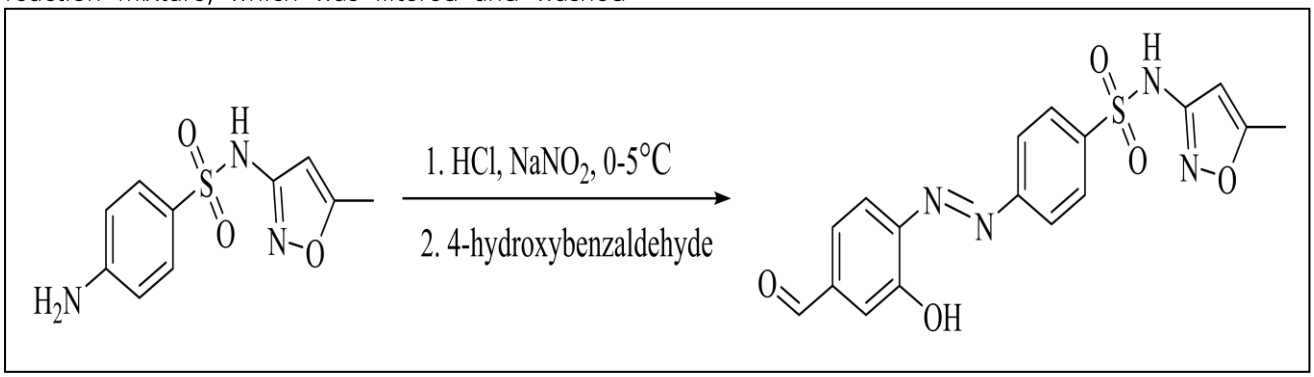
temperature (0-5°C) and kept overnight as a final step for the diazotization process. Brown reddish crystals of sulfamethoxazole azo was formed in the reaction mixture, which was filtered and washed using distilled water, then dried. melting point of azo dyes was recorded. The reaction was followed by a thin layer chromatography (TLC) technique.



Scheme1. Synthesis 4-((4-Formyl-2-Hydroxyphenyl) Diazenyl -N-(5-Methyl Isoxazol-3-yl(

Benzene Sulfonamide) (FDS).

Preparations of the standard solutions

Preparation of the metal ion solutions in concentration of (1×10^{-3} M) and have dissolved the weights within acceptable parameters within each of the salts previously mentioned [$CuCl_2.2H_2O$, $Pb(NO_3)_2$ and $HgCl_2$] through buffer solutions. Simultaneously, the range of concentrations are prepared using the reagent solutions which were formed through dissolving the convenient weight (FDS) by using ethyl alcohol.

Synthesis of Complexes

synthesis of all complexes were completed through adding (0.02 mole) of (FDS) ligand solution which was prepared in (1:1) mixture of ethyl alcohol and distilled water, with stoichiometry amount (0.01 mole) of Hg (II), Cu (II) chloride and Pb (II) nitrate salts separately being dissolved in buffer solutions at the desired acidic value pH within every metal ion. This mixture solution will continuously be stirred and kept overnight until coloration (dark orange) appears in solution. Filtered and washed using distilled water, dried, melting points of all complexes were recorded.

3. Results and discussion

The analytical results of complexes are given in Table1. All the chelate complexes have an ionic character and soluble in the most of organic solvents.

Table1. Some physical properties Data of (FDS) and its Complexes

Λm ($S.mol^{-1}.cm^2$) in Mixed of Ethanol and distilled water	M.P °C	Color	M.F.
----------	155-160	riddish – brown	$(C_{17}H_{14}N_4O_5S)$
44	240-245	Orange –brown	$Na_2[CuL_2Cl_2]$
47	190-195	Light brown	$Na_2[HgL_2Cl_2]$
55	210-216	Orange –brown	$Na_2[PbL_2(NO_3)_2]$

A variety of studies have been conducted on molar concentration (0.000005 – 0.0002 M) for (FDS) along with the metallic ion solutions. The concentrations (0.00001-0.0001M) are appropriated for Lambert Beer's law, which resulted in straight line Fig. 1.

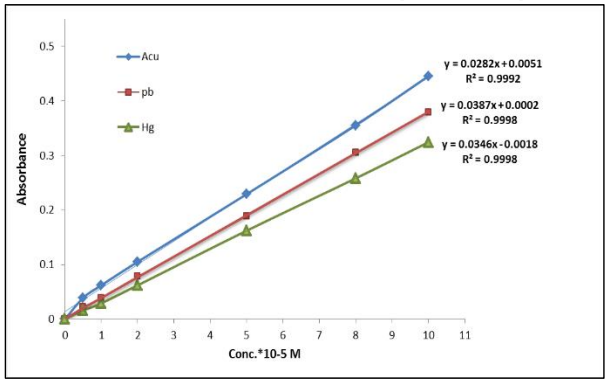


Fig.1The Linear Relations Between Absorbance and Molar Concentration.

Analysis was conducted on the desired pH value with the range (2-12), at (λ_{max}) for each complex, which were plotted on the graph as shown in Fig. 2.

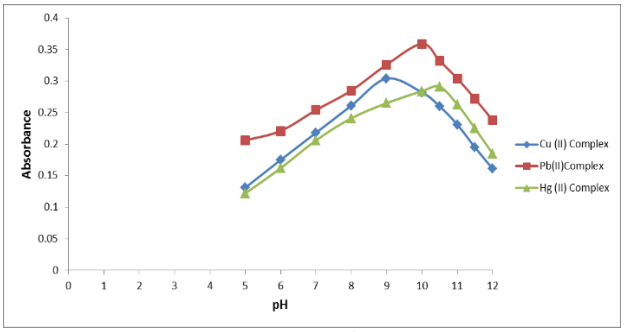


Fig.2 Optimal Acidic Value of Cu(II), pb(II) and Hg(II) Structures at (λmax) of Each.

Ratio of Metal - ligand [Metal : ligand]

This method necessitated the preparation of a set of solutions that contain various concentrations of moles within the reagent component solution (1×10^{-6}-1×10^{-4}M) with a fixed moles concentration of the metal ion solution (3×10^{-5}M). Subsequently, the absorbance of the complexes solutions was calculated accordingly to its respective wavelengths as well as its optimal acidic value for each of the metal ion complexes. However, the results have shown that the absorption only

occurred on the formed complex [20]. From the graph between the mole ratio on the x-axis and the absorbance on the y-axis, where the intersection point of the two straight lines towards the x-axis represents the mole ratio (metal: ligand) of the formed complexes, it was concluded that the ratio of the metal to ligand is 1:2 (metal-ligand) for all complexes as shown in Fig.3 . Stoichiometry of the kind ML2 and chelating reagent (FDS) behaves as a bidentate, coordinated with metallic ions by (N,O) to result a five-membered chelating ring and octahedral configuration [21] Fig.4.

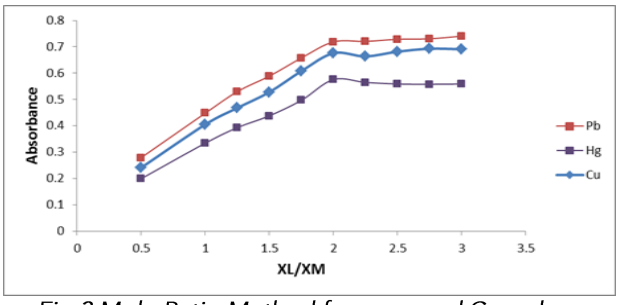


Fig.3 Mole Ratio Method for prepared Complexes Solutions.

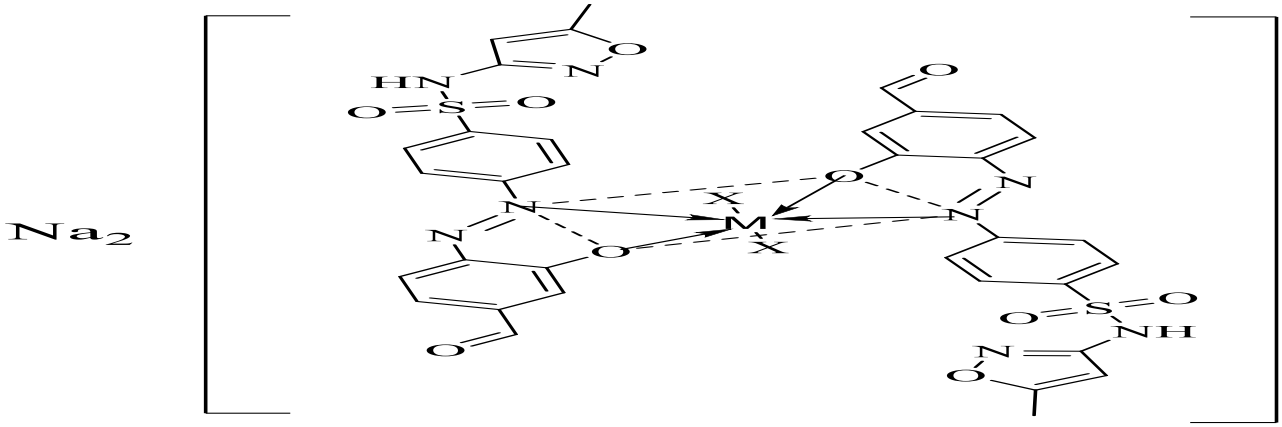


Fig.4 Proposed Configuration of Even the Formed Complexes.

Where X = Cl $^{-}$, NO^{3-}, M = Cu (II), Pb (II), Hg (II)

Estimation the Stability Constant (K) , Free Energy (ΔG),Enthalpy(ΔH) and Entropy(ΔS) of the Metal Complexes.

The following equation is used to calculate K for Cu (II), Pb (II) and Hg (II) complexes for a mole ratio (M: L) (1:2).

$K = (1-\alpha) / 4\alpha^3C^2$ (1)

$\alpha = A_m-A_s / A_m$

where α is the dissociation degree

A_s denotes the solution absorption at stoichiometric ligand with metal ion quantity.

A_m denotes solution absorption at the same volume of metal and excess of ligand.

C denotes the concentration of complex solutions at molar.

In order to calculate (K), the (Abs) will need to be known for the ligand and metal ion combined solutions in a specific (λ_{max}) and optimal pH of all metal ions [22]. The (K) value for complexity are shown in (Tabl.2). The complexes of (K) have the following sequence:

$Cu^{2+} > pb^{2+} > Hg^{2+}$

The sequence is in accordance to the Irving-Williams stability constant series [23].

The equation (ΔG = - RTLn K) is used to calculate Gibbs free energy (ΔG) where R = constant of gas = 8.314 $J.mol^{-1}$ k^{-1} ,T = absolute temperature (kelvin).

From Van Hoff equation :

Ln K = (-ΔH/RT) (2)

Calculated the value of (ΔH) and also (ΔS) was calculated from the following thermodynamic relationship :

G =ΔH -T ΔS (3)Δ

Table2. Optimal pH, Molar absorptivity,(K),ΔG , ΔH and ΔS of (FDS) and its Complexes at 298 k.

SΔ kJ. mol^{-1}	HΔ kJ. mol^{-1}	GΔ kJ. mol^{-1}	Ln K L^2mol^{-2}	Stability constant (K) L^2 mol^{-2}	Molar absorptivity L cm^{-1} mol^{-1}	Optimal pH	Compound
--------	----------	----------	---------	------	----	6-7	$(C_{17}H_{14}N_4O_5)$
0.212	-1.3469	-64.712	26.120	2.207×10^{11}	2540	9.8	$Na_2[CuL_2Cl_2]$
0.0923	-33.9476	-61.744	24.920	6.653×10^{10}	2455	10	$Na_2[PbL_2(NO_3)_2]$
-0.162	-109.944	-61.411	24.787	5.85×10^{10}	3050	10.5	$Na_2[HgL_2Cl_2]$

The results of the calculation of thermodynamic values showed that the coordination process is an spontaneous process (-ΔG) for all complexes, the formation reactions of copper (II), lead(II) and mercury(II) complexes are exothermic reactions (-ΔH). All complex preparation reactions are exothermic reactions and a positive value (ΔS). copper(II), lead(II) complexes refers to that the formation of divalent complexes (automatic), this leads the reaction towards the products [24], while a negative value (ΔS) of mercury(II) complex refers to that the formation of divalent complexes (not automatic), this leads the reaction towards the reactants.

1H NMR Spectrum

^{1}HNMR **spectrum** of (FDS) show the expected characteristic signals .The CH_3 proton gives singlet at δ 2.63 ppm, Also a multiples peak at δ 7.4 -7.9 ppm aromatic protons for and peak at δ 8.9 ppm to

aliphatic H of (C=O) aldehyde. In addition singlet peak at δ 9.7 ppm to (NH). Proton of OH shows resonates as a singlet at δ 9.3 ppm in case of ligand but this peak disappears in the complexes indicating the involvement of phenolic oxygen in the coordination by deprotonating [25]. Finally, the solvent signal appeared at δ 2.5 ppm return to (DMSO-*d6*) [26] .

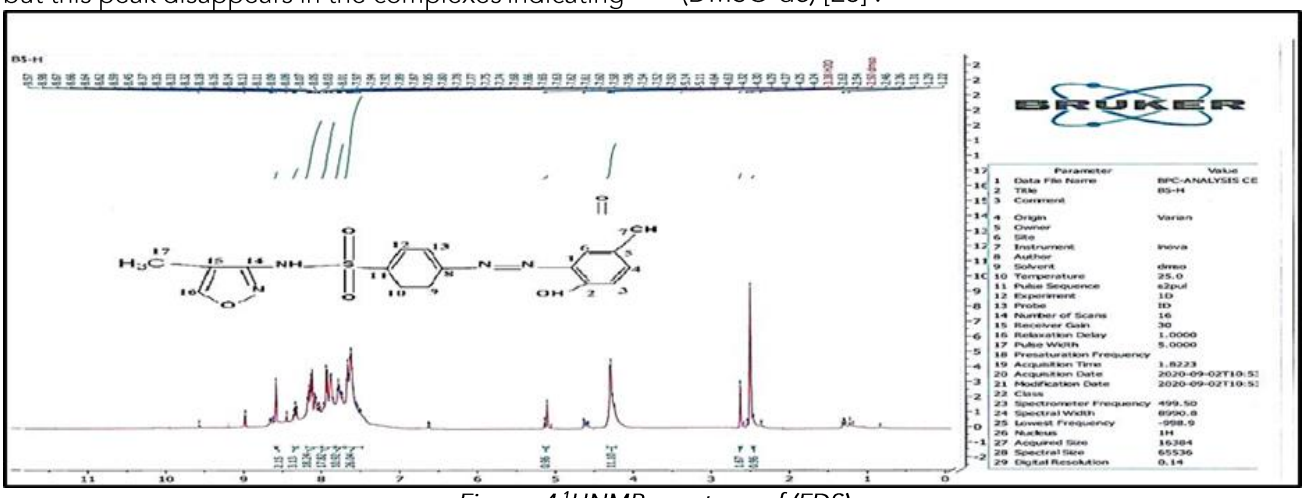


Figure. 4 ^{1}HNMR spectrum of (FDS)

Conclusion

The present study included the synthesis of ligand 4-((4-Formyl-2-Hydroxy Phenyl) Diazenyl)-N-(5-Methyl Isoxazol-3-yl) Benzene Sulfonamide (FDS) and their complexes easily after fixed optimum condition of concentration and acidic value , and mole ratio of ions (Cu^{2+}, Pb^{2+}, Hg^{2+}) with the possible structures. The complexes were generally prepared in strong basic medium.

The reagent behaves as bidentate and a five-ring formation, which increases the stability

of the complex formed and this is evidenced by the values of the formation

The results of the calculation of thermodynamic values constants obtained from this study.

showed that all complex preparation reactions are exothermic reactions , in addition to

. being spontaneous reactions

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References

Cai, K., He, H., Chang, Y., and Xu, W. [1] An efficient and green route to synthesize azo compounds through methyl nitrite". Green and Sustainable Chemistry,4(3) 2014.

[2] Martins, P., Jesus, J., Santos, S., Raposo, LR., Roma-Rodrigues, C., Baptista, P V., and Fernandes, "Heterocyclic anticancer compounds: recent advances and the paradigm shift towards the use of nanomedicine's tool box". Molecules, 20(9) 16852-16891(2015).

[3] Sarkar, S., Banerjee, A., Halder, U., Biswas, R., and Bandopadhyay, R. "Degradation of synthetic azo dyes of textile industry: a sustainable approach using microbial enzymes". Water Conservation Science and Engineering, 2(4) 121-131(2017).

[4] Bratovčić, A. " Photocatalytic degradation of organic compounds in wastewaters". Technologica Acta: Scientific/professional journal of chemistry and technology, 11(2) 17-23(2019).

[5] Ahmed, F., Dewani, R., Pervez, MK., Mahboob, SJ., and Soomro, SA., " Non-destructive FT-IR analysis of mono azo dyes". Bulg. Chem. Commun, 48(1) 71-77(2016).

[6] Kaur, H., Yadav, S., and Narasimhan, B. "Diazenyl derivatives as therapeutic and diagnostic agents acting on central nervous system". Central Nervous System Agents in Medicinal Chemistry (Formerly Current Medicinal Chemistry-Central Nervous System Agents), 15(1) 42-51(2015).

[7] Kaur, H., Yadav, S., and Narasimhan, B. "Diazenyl derivatives and their complexes as anticancer agents". Anti-Cancer Agents in Medicinal Chemistry (Formerly Current Medicinal Chemistry-Anti-Cancer Agents), 16(10) 1240-1265(2016).

[8] Hamzah, MA. M., Jebur, IK., and Ahmed, AK. , "Synthesis, Characterization and Biological Activity Evaluation of Some New Azo Derivatives from 2-Amino Benzothiazole and Their Derivatives". kirkuk university j. sci. stud., 13(1)212.227(2018).

[9] Velho, SR., Brum, LF., Petter, CO., dos Santos, JHZ., Šimunić, Š., and Kappa,WH. , "Development of structured natural dyes for use into plastics", Dyes and Pigments, (136) 248-254(2017).

[10] Ortiz-Monsalve, S., Dornelles, J., Poll, E., Ramirez-Castrillon, M., Valente, P.,and Gutterres, M. "Biodecolourisation and biodegradation of leather dyes by a native isolate of Trametes villosa". Process Safety and Environmental Protection, (109) 437-451(2017).

[11] Benkhaya, S., M'rabet, S., and El Harfi, A. "Classifications, properties, recent synthesis and applications of azo dyes", Heliyon, 6(1) 2020.

[12] Kamika, I., and Momba, MN. "Effect of vanadium toxicity at its different oxidation states on selected bacterial and protozoan isolates in wastewater systems", . Environmental technology,

35(16) 2075-2085 (2014). [13] Shankarling, GS., Deshmukh, PP., and Joglekar, AR. " Process intensification in azo dyes". J. Env Chem. Eng., 5(4) 3302-3308(2017).
[14] Lipskikh, OI., Korotkova, EI., Khristunova, YP., Barek, J., and Kratochvil, B., "Sensors for voltammetric determination of food azo dyes-A critical review",Electrochimica Acta, 260 974-985(2018).
[15] Yaseen, DA., and Scholz, M., "Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review", Int. j. Environ. Sci. Technol., 16(2) 1193-1226(2019).
[16] Chaturvedi, S. "Azo Dyes Decolorization Using White Rot Fungi",Res. Rev. J. Microbiol. Biotechnol., 8(2) 9-19 (2019).
[17] Singh, PK.,and Singh, RL. "Bio-removal of azo dyes: a review", Int. J. Appl. Sci. Biotechnol., 5(2)108-126(2017).
[18] Jadhav, I., Vasniwal, R., Shrivastava, D., and Jadhav, K. "Microorganism-based treatment of azo dyes", J. Environ. Sci. Technol, 9(2) 188(2016).
[19] Shibata, S., Furukawa, M.,and Nakashima, R. "Syntheses of azo dyes containing 4, 5-diphenylimidazole and their evaluation as analytical reagents", Anal. Chim. Acta., 81(1) 131-141(1976).
[20] Al-Adilee, K J. and Hesson, HM. "Synthesis, identification, structural, studies and biological activity of some transition metal complexes with novel heterocyclic azo-Schiff base ligand derived from benzimidazole," J. Chem. Pharm. Res., 7(8) 89–103, (2015).
[21] Petkevich, SK., and Potkin, VI., "Syntheses, structures and properties of magnetically active copper (II) compounds with 3-amino-5-(4-methylphenyl) isoxazole", (2018).
[22] Skoog, DA., West, DM., and Holler, FJ. An introduction to electrochemistry. Fundamentals of Analytical Chemistry, 7th edition. Saunders College Publishing, New York, 303-29(1988).
[23] Kostic, I., Andelkovic, T., Andelkovic, D., Nikolic, R., Bojic, A., Cvetkovic, T., and Nikolic, G. "Interaction of cobalt (II), nickel (II) and zinc (II) with humic-like ligands studied by the ESI-MS and ion-exchange methods", J. Ser. Chem. Soci. 81(3) 255-270 (2016). .
[24] GÜVENÇ A., KARABACAKOĞLU, B., KOÇKAR, ÖM., and PEKEL, AT., The synthesis of manganese (III) acetate in bipolar packed-bed and trickle-bed electrode cells. Turkish Journal of Chemistry, 24(1) 101-108 (2000).
[25] Xu, H., Fan, GP., Liu, Z., and Wang, GW. "Catalyst-and solvent-free mechanochemical synthesis of isoxazoles from N-hydroxybenzimidoyl chlorides and enamino carbonyl compounds", Tetrahedron, 74(45) 6607-6611(2018).
[26] Ibrahim, SA., Al-Tawash, BS., and Abed, MF., "Environmental assessment of heavy metals in surface and groundwater at Samarra City, Central Iraq,". Iraqi J. Sci., 59(3A) 1277-1284(2018).