Study the Effect of Magnetized Water on Some of the Chemical Parameters for EBT Complexes with Some of M^{2+} Ions

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Summary: In this paper, the effect of magnetized water on the stability constant Kst, oscillation strength *f*, molar extinction coefficient ε_{max} and Gibbs free energy ΔG for complexes was investigated. Complexes of Eriochrome black T (EBT) as a ligand with Ca^{2+}, Mn^{2+}, and Zn^{2+} ions were prepared for this purpos. The stability constant values of the complexes found to be decreased by using magnetic water in their preparation except for EBT-Ca complex. Both Ca^{2+} and Mn^{2+} ions showed deviation from Irving-Williams order. The oscillation strength shows the type of spectrum is absorption spectrum for all complexes and in both in magnetized and non-magnetized water. ε_{max} found to be increased by using magnetized water over than non-magnetized water. The stability constants for the complexes calculate analytically by applying jobs method and Yoe and Jones method.

Keywords: EBT complexes; Magnetized water; Oscillation strength in the magnetic field; Stability constant.

Introduction

Water can be classified as one of the most important and common materials in the earth because of the living of all organisms dependent on the existence of water. The growth and developments of human beings in agriculture and industrial beside the growth of animals and plants lead to increase the demand for water. So it's very important to study the properties of water and important to know most of these properties can be changed under the influence of magnetic field, besides we cannot know the molecular structure of water under the affected rules of the magnetic field [1-9]. The water which is exposed to magnetic field calls magnetized water this type of water can be obtained by exposing the water to the magnetic field to influence some of the chemical and physical interchanging in water. This process is low cost, doesn't require energy and environmental friendly. Recently magnetized water used in agriculture, medicine, environmental and medicine fields [10-12]. Many studies since 1980 were carried out to understand the effect of the external magnetic field on water these studies showed the properties such as oxygen vaporization rate and air environment significantly changed under the effect of the external magnetic field [13]. The size of water clusters which is one of the liquid water aspects found to be changed by applying external magnetic field [14-15]. The dissolution rate of some materials like copper sulphate and oxygen in water found to be accelerating by applying magnetic field [16-17]. Water Refractive index found to be increased approximately by %0.1 according to Hosoda *et al.*,measurements at atmospheric pressure and under influence of magnetic field up to 10 T which indicates increase the stability of hydrogen bonding [18]. Promoting of hydrogen bonding also confirmed by Inaba *et al.*,[19].Dissolving rate of minerals and acids can be increased by applying magnetic field [20].the presence of external magnetic field leads to rearranging the angle between hydrogen and oxygen in the molecule of water which is reduced from 104.45◦ to 103◦ [21]. Strong magnetic field 1-10 T lead to some disturbance to hydrogen bonding and promote mobility of salt [22]. Evaporation rate showed the increase in low magnetic field 15 mT [23]. The melting point of water raised 5.6mK at 6 Tand for heavy water raised to 21.8mK at 6T [19], while the transition of sol-gel lowering at 0.3T and 3C◦ in methylcellulose [24]. The order structure of water around the colloids molecule and hydrophobic and the fluorescence of probes dissolved in water found to be increased in a static magnetic field [25-26]. Infrared spectrum found to be changed in a static magnetic field due to the effected of water cluster and this effected remain for the period time even after removing the external magnetic field [27]. Gases solubility in seawater increased even in small magnetic field 20-50 μT [28]. Some reactions dependent proton transition may be accelerating because of increasing proton spin relaxation under the effect of the magnetic field [29]. Magnetic water prevents the absorption of harmful metals such as nickel and lead by roots beside the uptake percentage of nutrient elements such as potassium, zinc, and phosphorus are increased [30].to enhance the plants yield its recommended to irrigation the plants by magnetized water because it will increase water efficiency and productivity [31-32]. Germination speed is increased by irrigation with magnetized water [33]. Eriochrome black T (EBT) Fig -1 of the

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IUPAC name is 1-[1-hydroxy- 2-naphthol azo]-6-nitro -2-Naphthol- 4-sulphonic acid sodium salt is an anionic organic compound possess molecular formula $C_{20}H_{12}N_3NaO_7S$ and molecular weight 461.38 gm/mol. This compound was used as an indicator and to make a complex with different metal ions. The aim of this paper is to study the effect of magnetic field on the stability constants for complexes formed between EBT and different metal ions by using normal and magnetized water under the same conditions.

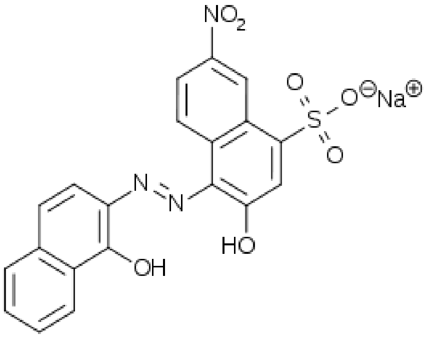

Fig. 1: Structure of Eriochrome black T (EBT).

Experimental

Instruments & Chemicals

Electronic Spectra of the EBT-M complexes were recorded by U.V – visible Spectrophotometer (Shimadzu U.V-1800 Double puma). Magnetized water was prepared by using a magnetic ring type CMS WTS-100 with the intensity of 4800 gauss. Beckman Zeromatic RSS-3 pH meter used for adjusting the pH of solutions**.** All chemicals were collected from Merck and Fluka companies.

Preparation of Solutions of EBT-M Complexes

Solutions of concentration 10^{-3} mol/L were prepared for EBT, Ca^{2+}, Mn^{2+} and Zn^{2+} ions respectively. The pH of the buffer was adjusted to be 10 by using ammonium chloride and ammonium hydroxide [34]. Two sets of working solutions were prepared first one in molar ratio of 1:1:1 by mixing 1ml of EBT, pH solution and metal ion respectively the second one was prepared in molar ratio of 1:1:3 by mixing 1ml of EBT, 1ml of pH solution and 3ml of metal ion respectively. The volumes of the solutions were completed to 50 ml by using non-magnetized water. The absorbance of the solution was recorded after 30 min to achieve maximum absorption A_{max} at λ_{max} (Table-1) for the complex in non-magnetized water [35]. Magnetized water was prepared by passing the water through a magnetic ring type CMS WTS-100 with intensity of 4800 gauss for 1 hour and flow rate of 20 ml/s the same procedure for the preparation of working solutions by using non-magnetized water were repeated the same process and then diluting the solution with magnetized water instead of non-magnetized water. The values of A_{max} were recorded to be compared

Results and Discusion

Electronic Spectra

The electronic absorption spectra of the EBT-M complexes were recorded at room temperature using magnetized and non- magnetized water as a solvent. The absorption bands with their transition are listed in Table -1 and their spectra are shown in Fig 2. EBT-Ca, EBT-Mn, and EBT-Zn complexes showed absorption bands corresponding to charge transfer bands (C.T) L → M and intraligand filed due to bathochromic shift [36-37]. The electronic spectrum of the EBT-Mn complex shows two absorption bands at the region (1620 - 17241) cm^{-1} and (29551 - 32680) cm^{-1} which are assigned to ${}^6A_1g \rightarrow {}^4T_1g$ (p) and ${}^6A_1g \rightarrow {}^4T_1g$ (G) respectively [38].

Table-1: Electronic spectrum and electron transitions for EBT-M complexes in magnetized and non-magnetized water.

Symbol of complex	Maximum absorption In ratio 1:1:1 (λ_{max} nm); υ_{max} cm^{-1}		Maximum absorption In ratio 1:1:3 (λ_{max} nm); υ max cm^{-1}		Band assignment
	H_2O	H_2O Mag.	H_2O	H_2O Mag.	
EBT-Ca	(198) 50505	…..	….	……	$\pi \rightarrow \pi^*$ (Intraligand)
	(297) 33670	…..	…..	……	
	(340) 29412	(427) 23419	(340) 29412	(343) 29155	
	(555) 18018	(552) 18116	(553) 18083	(553) 18083	L → M (C.T)
EBT-Mn	(197) 50761	……	……	……	$\pi \rightarrow \pi^*$ (Intraligand)
	(335) 29851	……	(306) 32680	……	${}^6A_1g \rightarrow {}^4T_1g$ (G)
	(612) 16340	(606) 16501	(580) 17241	(615) 16260	${}^6A_1g \rightarrow {}^4T_1g$ (p)
EBT-Zn	(294) 34014	……	……	(293) 34130	$\pi \rightarrow \pi^*$ (Intraligand)
	(343) 29155	(344) 29070	(344) 29070	(344) 29070	
	(558) 17921	(560) 17857	(560) 17857	(560) 17857	L → M (C.T)

*H_2O = non-magnetized water; H2O Mag. = magnetized water

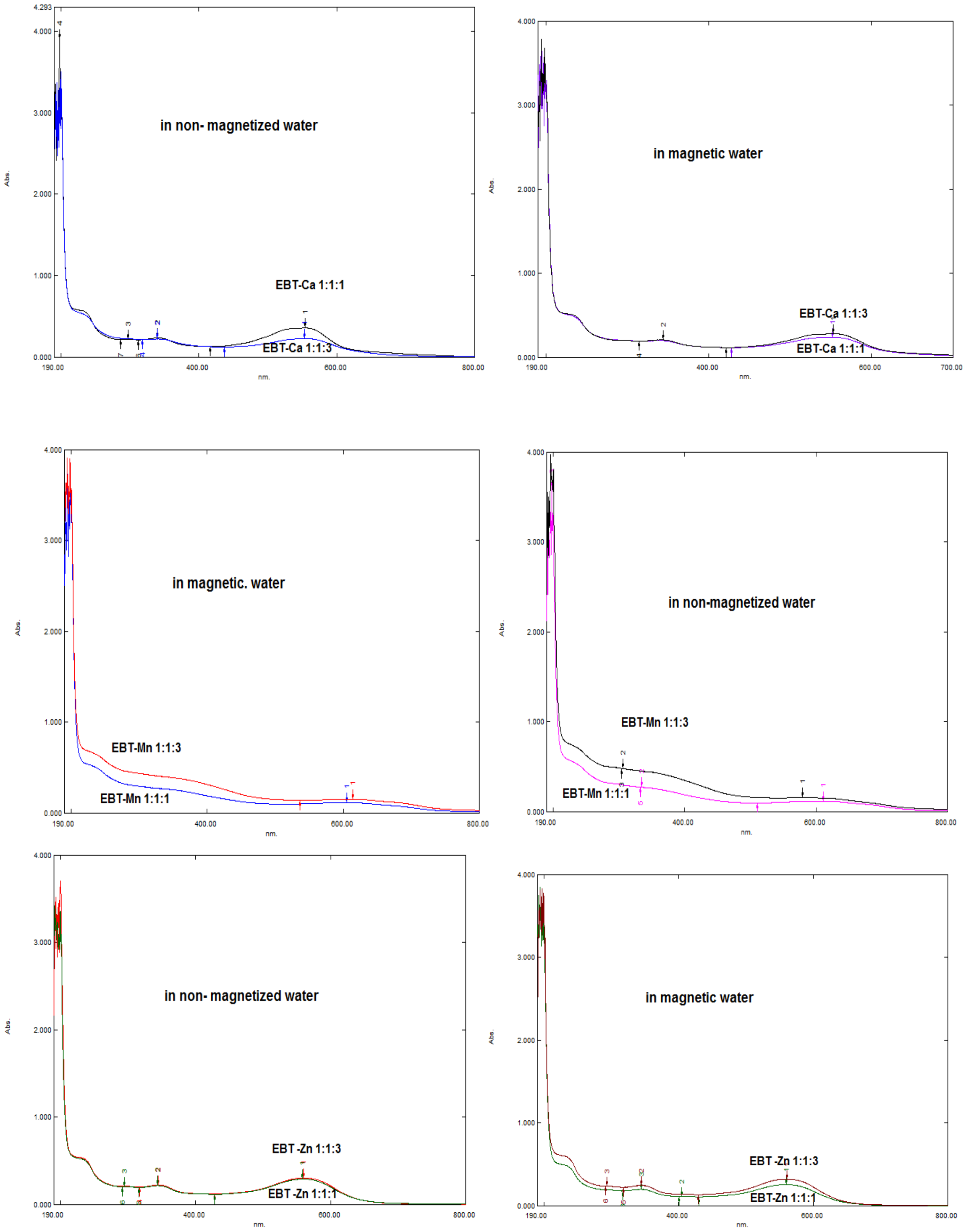

Fig. 2: Electronic spectra of EBT-M complexes for Ca^{2+}, Mn^{2+} and Zn^{2+} ions in magnetized and non-magnetized water.

Stability Constant of EBT-M Complexes

The complex reactions follow the equation

$$mM + nLy \longleftrightarrow MmLn$$

$$m\alpha C \quad n\alpha C \qquad (1-\alpha)C$$

where M and L are the metal ion and ligand respectively while, m and n represent the number of moles of metal and ligand, α represent a degree of dissociation and C represents the concentration of solutions. As long as the values of C, m and n are known then we can calculate the stability constant (Kst) for the complex by using the equation (1).

$$Kst = (1-\alpha) / m^{m} . n^{n} . (\alpha)^{m+n} . (C)^{m+n-1} \qquad (1)$$

There are two methods to calculate the value of a degree of dissociation jobs method and Yoe and Jones method.

Jobs method

In this method Fig 3 the absorbance was plotted versus the ligand mole fraction (X) = $C_L/C_M + C_L$. The stoichiometric mole fraction (SMF) can be calculated from the curve at maximum absorbance. X_{max} = SMF = n/n+m. the curve in the plotting indicates that the complex is in the dissociation state. The value of α can be estimated from the absorbance as below

$$A_{\alpha} = A_{o} - A_{max} \qquad (2)$$

where A_{max} represent the maximum value of complex absorbance, A_o it's the absorbance refers to the intercept of expanded lines attached to the curve and A_α represent the absorbance value at partial dissociation of the complex from the known A_α value we can calculate α by using the equation

$$\alpha = A\alpha / \varepsilon . C. b \qquad (3)$$

where ε represent extinction coefficient, C is the concentration of the complex and b the thickness of the absorbance cell. By applying the values of α in equation (1) the stability constant can be calculated.

Yoe and Jones method

In this method Fig 4 the absorbance was plotted versus the ligand mole ratio (r) = C_L/C_a

There values of A_α, A_o, A_{max} and α calculated to the same way in jobs method and the value of stability constant can be calculated by using equation (1). The values of stability constant at the non-magnetized and magnetized water where calculated as shown in the Table-2.

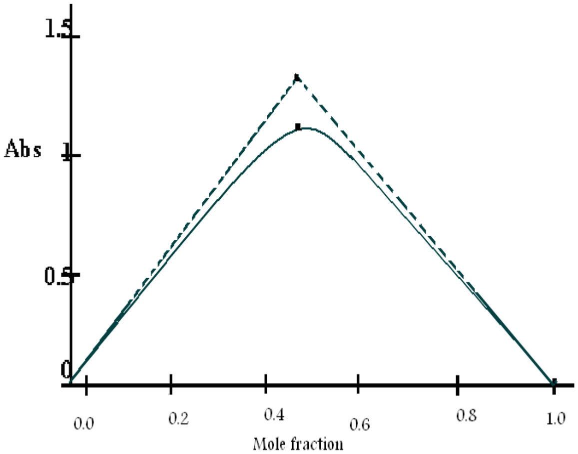

Fig. 3: Absorbance vs ligand mole fraction.

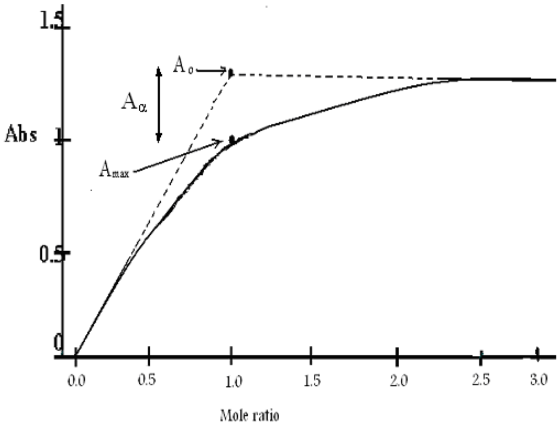

Fig. 4: Absorbance vs ligand mole ratio.

When electromagnetic radiation interacts with atom or molecule three processes can be occurs first one according to classical oscillating for charge distribution the atoms emitting radiation spontaneously this can be occur only if the atoms were in state with higher energy, the second process occur when the atom or molecule absorbs radiation with energy enough to transfer to higher energy state and the third process may occur due to emission of photons under the effect of radiation field this process is called stimulated emission. The intensity of transition between two states (a and b) can be characterized by oscillating strength if the oscillating strength $f_{ba} > 0$ then the process is absorption, while if $f_{ba} < 0$ the process is emission [35]. The transition oscillation strength *f* which can be defined as the ratio of polarization of molecule or atom to the polarization of electron in the vacuum was calculated for all metal-complex according to the equation.

$$f=6.78* 10^{-9} * \varepsilon_{max} *\upsilon \qquad (4)$$

Where ε_{max} is the molar extinction coefficient ($mol^{-1}.L.cm^{-1}$) and υ is full width at half maximum FWHM (cm^{-1}). These values were calculated for both magnetic and non-magnetized water Table-1. Standard Gibbs free energy ΔG (kj/mol) for normal and magnetized water where calculated through the equation

$$\Delta G = -R\ T\ \ln K \qquad (5)$$

From the data (Table-2) we can see the value of stability constant for all of EBT –M complexes increase in non-magnetized water as the atomic number increase, for EBT- Ca complex according to Jeffery *et al.*,the color of Ca complexes is due to charge transfer from ligand to metals and these complexes are relatively unstable in aqueous solutions [30], also according to Irving-Williams order the stability constant systematically decrease as the atomic number is increase except for Cu^{2+} (due to jahn teller effect) also the effect of ligand field for transition metals. The Irving-Williams series for M^{+2} ions can represent as.

$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

The values for stability constants for EBT-M complexes by using magnetized water show decrease compared with the corresponding complexes in non-magnetized water except for EBT- Ca complex. This decrease may be due to the fact that presence of static applied magnetic field can reduce mobility of the solvent also the effective interaction increase which leads to decrease of diffusivity and the solvent become block diffusion of solute molecules, besides the magnetic field reduce the volume of solvent and increase vdW interaction and hydrogen bond strength this lead to change in solvents radial distribution function [36]. Standard Gibbs free energy ΔG for all complexes was possessed negative charge that indicates the reaction is endothermic in both normal and magnetized water.

Conclusion

The stability constants for the EBT complex with Ca^{2+}, Mn^{2+} and Zn^{2+} ions when prepared in a non-magnetized water solution were found to be decreased as the radii of an ion decreased, these results are in agreement with Irving-Williams order, while the stability constants values showed a decrease when the complexes were prepared in magnetized water except for the Ca complex. The Ca complex showed stability in a magnetic water solution versus an unmagnified water solution.This effect may it happen due to the influence of magnetic field on the properties of water such as increasing the effective interaction that will lead to decrease the diffusion of the solute molecule in the solvent [36]. EBT-Ca and EBT-Mn complexes show deviation from Irving-Williams order in magnetized water where the stability constant for both ions show more stability in accordance with and Zn^{2+} ions which possess larger radii than Ca^{2+} and Mn^{2+} respectively[37]. This may be due to The stability of EBT-Zn complex found to be decreased in magnetized water over than non-magnetized water because the large size of Zn ion in compare with decreasing size of the complex due to increasing of hydrogen bonds therefor, the ratio of ion to molecules become larger and the stability becomes less. For the same reason, the stability constants for the other ions found to be inversely proportional to the size of a metal ion. Gibbs free energy values are proportional to stability constants and possess negative charge for all complexes this indicates the reaction is endothermic. The oscillating strength characterized the transition intensity between two states oscillating strength $f_{ba} > 0$ then the process is absorption, while if $f_{ba} < 0$ the process is emission, so the processes for all complexes in both magnetized and unmagnified water are absorption.

Table-2: Effect of magnetic field on the values of stability constant, molar coefficient, FWHM, oscillation strength and Gibbs free energy for EBT- M complexes.

Symbol of complex	$\log K_{st}$ H_2O	$\log K_{st}$ H_2O Mag	$\varepsilon_{max.}$ $mol^{-1}.L.cm^{-1}$ H_2O	$\varepsilon_{max.}$ $mol^{-1}.L.cm^{-1}$ H_2O Mag.	υcm^{-1} H_2O	υcm^{-1} H_2O Mag.	f H_2O	f H_2O Mag.	ΔG KJ/mol H_2O	ΔG KJ/mol H_2OMag.
EBT-Ca	**4.70**	**6.23**	**241.5**	**245.6**	**10435000**	**91130**	**0.17**	**0.15**	**-26.80**	**-35.50**
EBT-Mn	**5.80**	**5.47**	**110.7**	**116.0**	**105870**	**77140**	**0.08**	**0.06**	**-33.09**	**-31.02**
EBT-Zn	**6.80**	**5.30**	**203.3**	**229.0**	**92330**	**93980**	**0.13**	**0.15**	**38.80-**	**30.24-**

*H_2O = non-magnetized water; H_2O Mag. = magnetized water

References

1. R. Ohata, N. Tomita, and Y. Ikada, Effect of a static magnetic field on ion transport in a cellulose membrane, *J. Colloid Interf Sci.*, **270**, 413 (2004).
2. Bour, PCluster model of liquid water and its IR spectroscopic response, *ChemPhysLett.*, **365**, 82 (2002).
3. A. C. Ji, X. C. Xie and W. M. Liu, Quantum magnetic dynamics of polarized light in arrays of microcavities, *Phys Rev Lett*, **99**, 183602 (2007).
4. Z. D. Li, Q. Y. Li and L. Li, and W.M. liu, Soliton solution for the spin current in ferromagnetic nanowire, *Phys Rev E.*, 76, 026605 (2007).
5. K. Higashitani, J. Oshitani, and N. Ohmura, Effects of magnetic field on water investigated with fluorescent probes Colloids Surf A, *PhysicochemEng Aspects.*, **109**, 167 (1996).
6. M. C. Amiri, and A. A. Dadkhah, On reduction in the surface tension of water due to magnetic treatment. Colloids Surf A: *PhysicochemEng Aspects.*, **278**, 252 (2006).
7. K. T. Chang, and C. I.Weng, The effect of an external magnetic field on the structure of liquid water using molecular dynamics simulation, *J Appl Phys.*,100 043917-043922 (2006).
8. B. N. KeLaXin, Magnetization of Water (in Chinese), Measurement Press, Beijing, **78** (1982).
9. D. C. Yang, and L. L. Yang, Magnetization of water and magnetized water (in Chinese), *BiolMagn.*, 3, 20-25 (2000).
10. Y. Ali, R. Samaneh, F. Kavakebian. Applications of Magnetic Water Technology in Farming and Agriculture Development, A Review of Recent Advances, *Current World Environment.* **9**, 695 (2014).
11. A. Yadollahpour, S. Rashidi, Z. Ghotbeddin. Electromagnetic Fields for the Treatments of Wastewater: A Review of Applications and Future Opportunities, *J Pure Appl Microbio.*, 8, 3711 (2014).
12. Ali Y, Samaneh R, Zohre R, Mostafa J. Magnetic Water Treatment in Environmental Management: A Review of the Recent Advances and Future Perspectives. *Current World Environment.*, **9,** 1008 (2014).
13. J. Nakagawa, N. Hirota, K. Kitazawa, and M. Shoda, Magnetic field enhancement of water vaporization, *J. Appl. Phys.*, **86**, 2923 (1999).
14. S. H. Lee, M. Takeda, and, K. Nishigaki. Gas–Liquid Interface Deformation of Flowing Water in Gradient Magnetic Field –Influence of Flow Velocity and NaCl Concentration, *Jpn. J. Appl. Phys.*, Part 1 **42**, 1828 (2003)
15. M. Iwasaka, and S. Ueno, Structure of water molecules under 14 T magnetic field, *J. Appl. Phys.*, **83**, 6459 (1998).
16. N. Hirota, Y. Ikezoe, H. Uetake, J. Nakagawa, and K. Kitazawa, Magnetic Field Effect on the Kinetics of Oxygen Dissolution into Water, *Mater.Trans JIM.*, **41**, 976 (2000).
17. K. T. Chang and C. I. Weng, The effect of an external magnetic field on the structure of liquid water, *J. Appl. Phys.*, 100, 043917 (2006).
18. H. Hosoda, H. Mori, N. Sogoshi, A. Nagasawa, and S. Nakabayashi, Refractive Indices of Water and Aqueous Electrolyte Solutions under High Magnetic Fields *J.Phys.Chem.* A., **108**, 1461 (2004).
19. H. Inaba, T. Saitou, K. Tozaki, and H. Hayashi, Effect of the magnetic field on the melting transition of H2O and D2O measured by a high resolution and supersensitive differential scanning calorimeter, *J. Appl. Phys*., **96**, 6127 (2004).
20. J. D. Moon and H. S. Chung, Acceleration of germination of tomato seed by applying an electric and magnetic field, *J. Electro-Statistics.*, **48**, 103 (2000).
21. M. V. and H. Reminick, Effects Of Naturally Magnetized Water On Increasing Organic Bioenergy And Function Explore For Professional, **10**, 4 (2001).
22. K. T. Chang and C. I. Weng, An investigation into the structure of aqueous NaCl electrolyte solutions under magnetic fields, *Comput. Mat. Sci.*, **43**, 1048 (2008).
23. L. Holysz, A. Szczes and E. Chibowski, Effects of static magnetic field on water and electrolyte solutions, *J. Colloid Interface Sci.*, **316**, 996 (2007).
24. Q. Wang, L. Li, G. Chen and Y. Yang, Effects of magnetic field on the sol-gel transition of methycellulose in water, *Carbohydr. Polymers*., **70**, 345 (2007).
25. S. Ozeki, C. Wakai and S. Ono, Is a magnetic effect on water-adsorption possible, *J. Phys. Chem*., **95**, 10557 (1991).
26. K. Higashitani, J. Oshitani and N. Ohmura, Effects of magnetic field on water investigated with fluorescent probes, *Colloids Surf.*, A. 109, 1167 (1996).
27. A. Aladjadjiyan, Physical Factors for Plant Growth Stimulation Improve Food Quality. Food Production-Approaches, Challenges and Tasks, Publisher InTech., 145 (2012).
28. M. Khoshravesh, B. Mostafazadeh Fard, S. Mousavi, A. Kiani, Effects of magnetized water

on the distribution pattern of soil water with respect to time in trickle irrigation. Soil Use and Management. **27**, 515 (2011).

29. M. Al-Khazan, B. M. Abdullatif, N. Al-Assaf, Effects of magnetically treated water on water status, chlorophyll pigments and some elements content of Jojoba (Simmondsia chinensis L.) at different growth stages. *African Journal of Environmental Science and Technology*. **5**, 722 (2011).
30. Ijaz Nu-S, T. Hussain and R. Jamil, editors. Controlled Magneto-Electrochemical Generation of Ni Nano Particles. Meeting Abstracts, *The Electrochemical Society*. (2012).
31. X. Pang and B. Deng, Infrared absorption spectra of pure and magnetized water at elevated temperatures, *Europhys. Lett*,. **92**, 65001 (2010).
32. A. Pazur and M. Winklhofer, Magnetic effect on CO_2 solubility in seawater: A possible link between geomagnetic field variations and climate, *Geophys. Res. Lett*., **35**, L167 (2008).
33. H. E. L. Madsen, Crystallization of calcium carbonate in magnetic field in ordinary and heavy water, *J. Cryst. Growth*. **267**, 251 (2004).
34. G, H. Jeffery, J. Bassett, J. Mendham and R. C. Denny, Vogel's textbook of quantitative chemical analysis. Longman Singapore publishers pte.Ltd, 5th edition, 36 (1989).
35. D. A. Skoog, «Fundamentals of analytical chemistry», 5th Ed., John-Wiely and Sons, New York, London, pp 186 (1988).
36. B. N. Figis, «Introduction to ligand Field», John-Wiely and Sons,Inc., New York, London. (1966).
37. A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier Publishing Company New York, London (1968).
38. A. M. Rawaa, Preparation and Characterization of New Mixed Ligand Complexes of (p-Methyl Anilino)-p-Chloro Phenyl Acetonitrile and Ethylene Diamine, *Iraqi Journal of Science.* **57**, 2522 (2016).
39. Heiko Appel, thesis, graduate, *Oscillator strength from time-dependent density functional theory*, Msc. school-new Brunswick Rutgers, the state university of New Jersey, 14 (1999).
40. F. Moosavi and Mostafa Gholizadeh, Magnetic effects on the solvent properties investigated by molecular dynamics simulation. *Journal of Magnetism and Magnetic Materials.* **354**, 239 (2014).
41. Pang XiaoFeng and Deng Bo, investigation of changes in properties of water under the action of magnetic field, *Sci china Ser G-phys Mech Astron*., **51**, 1621 (2008).