Preparation and Adsorption of [Bis(1,10-phenanthroline) nitratolead(II)]nitrate Complex on Activated Carbon and Zeolite Surfaces

Barakat A. F. Kamel
Department of Chemistry, College of Science, University of Al- Mustansiriya, Baghdad-Iraq.
E-mail: baraka19832012@yahoo.com.

Abstract

In this research the complex [Bis(1,10)-phenanthroline) nitratolead (II)] nitrate was prepared and the adsorption of the complex on (activated carbon, zeolite and mixture of them) was studied in equal weights under various conditions such as: temperature, contact time, pH and the change in the weights of adsorbents. With respect to activated carbon, the adsorption quantity was increased at: (30-50)C^0 and (60-90) min, the suitable weight of activated carbon for adsorption was (0.15)g at pH (9). Zeolite, the adsorption quantity was increased at the temp. reached (50)C^0 in a contact time lower than (90) min at a critical weight (0.3)g and pH(9). Finally when both adsorbents were mixed, the adsorption quantity was increased at temp. reached (50)C^0 with the range of time (60-90) min in a weight (0.25)g at the range of pH(5-11).

Keywords**:** 1,10-phenanthroline, complex, Adsorption, Activated Carbon and Zeolite.

Introduction

1,10-Phenanthroline is a heterocyclic organic compound. As a bidentate ligand in coordination chemistry, it forms strong complexes with most metal ions[1]. 1,10-phenanthroline (Fig.(1)) represents one of the most frequently used chelate ligands in inorganic chemistry, but a detailed quantum chemical study of its vibrational spectrum has not yet been carried out. This is somewhat surprising since the molecule is only of moderate size and such an investigation would be of great value for studies on complexes, in which the intra-ligand vibrations of 1,10-phenanthroline must be clearly identified and separated (if possible) from the rest of the vibrational spectrum[2,3].

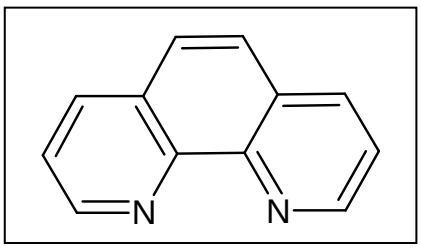

Fig.(1) The Chemical Structure of 1,10-Phenanthroline.

The coordination chemistry of pb (II) with N-donor ligand has been investigated in the past decade and frequently discussed in regard of the stereo chemical activity of the lone pair of electrons [4]. (J. Peric, M. Trgo, N. Vukojevic Medvidovi, 2004) studied the adsorption on zeolite by uptake of zinc and copper from aqueous solutions and confirmed that the efficiency of removal is higher for Cu than for Zn ions [5]. In the present paper, the existence of active sites on the carbon phase, which are able to combine with protons and ions are explicitly assumed. The proton and the ions are sorbed mainly by combination with these functional groups. This should explain the high selectivity of the activated carbon for protons and ions with respect to the not complex able cations, which has been experimentally observed. The active groups are considered exactly as ligands in solution [6]

Experimental

Materials

All chemicals used for the present study were of high purity reagent grade quality which include: 1, 10-phenanthroline (sigma/Aldrich), $Pb(NO_3)_2$ (BDH), Absolute ethanol(99.9%) (BDH), NH_4OH 10% and distilled water. Activated Carbon & zeolite: Thomas Baker Co., the diameter of sieve hole = 75µm

Instruments

UV-Vis.spectrophotometer (Model: CARY 100, VARIAN Co.) in the (200-800) nm regions, FTIR spectrophotometer (Model:

SHIMADZU) in the (400-4000)cm^{-1} regions, conductivity meter (Model: WTW F56) with platinum electrode, atomic absorption spectrophotometer (Model: phoenix-986-BEM Co., LTD.(UK)) and shaking water path (Model: BS-11 degetal, JEIO Korea, TECH.

Preparation of Complex

The complex [Bis(1,10-phenanthroline) nitratolead (II)] nitrate were synthesized by refluxing 25ml ethanolic solution of (1mmole, 0.331g) of the mentioned metal salt ($pb(NO_3)_2$) with 25 ml ethanolic solution of (2mmole, 0.36g) of ligand (1,10-phenanthroline), Few drops of NH_4OH solution were added and the mixtures were refluxed for 3 hours. The obtained products (white precipitate) were filtered, washed several times with hot ethanol until the filtrate becomes colorless and dried; the melting point of the complex are above $300C^0$.

Calibration Curve Determination

The determination of calibration curve was carried out for [Bis(1,10-phenanthroline) nitratolead (II)] nitrate complex by preparation of several solutions in different concentrations at constant wave length (λ_{max}= 344nm). The absorbance for these solutions were recorded in (Table (1)):

Table (1)
Initial concentrations and absorbance values for [Bis(1,10-phenanthroline) nitratolead(II)]nitrate complex at λ_{max}=344nm.

Concentration (ppm)	*Absorbance*
5	**0.02**
10	**0.0276**
15	**0.04**
20	**0.055**
25	**0.067**
30	**0.0756**
35	**0.0901**
40	**0.1008**

The relation between absorbance and concentration was carried out according to (Bear-Lambert Law): (A=ε.b.c), which showed a linear relation, its slope represents the molar absorbance coefficient ($\varepsilon=2\ 10^{-3}$) (Fig.(2)) shows this relation:

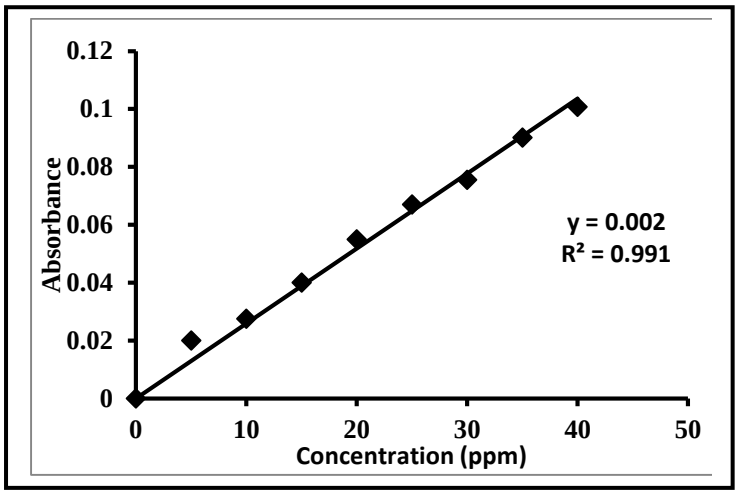

Fig. (2) Calibration curve for [Bis(1,10-phenanthroline) nitratolead (II)] nitrate complex.

Adsorption Study
-Effect of Temperature

Measurements for the effect of temperature on adsorbent performance used (0.1gm) adsorbent added to fixed volume of lead complex solution (10ml) of (10ppm) in six bottles, bottles were shaken for (1 hour) at (25, 30, 35, 40, 45 and 50)C^0 in shaking water bath at rotation of (120) turns and then the mixtures were filtered to get rid of adsorbent and

to get clear solutions. The absorbance was measured for each solution by UV-Vis. Spectrophotometer [7].

-Effect of Contact Times:

Times effect were measured on adsorbent performance used (0.1gm) adsorbent added to fixed volume of lead complex solution (10ml) of (10ppm) to six bottles, bottles were shaken at $30C^0$ and at (30, 60, 90, 120, 150 and 180) minutes in shaking water bath, at rotation of (120) turns and then the mixtures were filtered to get rid of adsorbent and to get clear solutions. The absorbance was measured for each solution [7].

-Effect of Adsorbent Weights:

Measurements of the effect of change in adsorbent weights on adsorbent performance by used fixed volume of lead complex solutions (10ml) of (10ppm) to six bottles, bottles were shaken at ($30C^0$) and a (0.05, 0.1, 0.15. 0.2, 0.25 and 0.3) gm in shaking water bath, at rotation of (120) turns and then the mixtures were filtered to get rid of adsorbent and to get clear solutions. The absorbance was measured for each solution [7].

-Effect of pH:

Measurements of pH effect on adsorbent performance was carried on by using (0.1gm) adsorbent added to fixed volume of lead complex solutions (10ml) of (10ppm) to five bottles, bottles were shaken at ($30C^0$) and at pH(2, 5, 7, 9 and 11) in shaking water bath, at rotation of (120) turns and then the mixtures were filtered to get rid of adsorbent and to get clear solutions. The absorbance was measured for each solution [7].

Results and Discussion

Conductivity Data

The molar conductance was determined by taking 0.1M of the complex [Bis(1,10)-phenanthroline)nitratolead (II)] nitrate in DMSO solvent, the measurement showed that there is a large difference between the molar conductance value of DMSO (315 µS. mol^{-1}) and the molar conductance of complex (357 µS. mol^{-1}) which reflects that the complex is electrolyte. From that, it can be deduced that one of nitrate molecule is present out of the coordination sphere and the other nitrate molecule is present in the coordination sphere [8].

Mole Ratio Measurements

The mole ratio measurements showed that the ratio of [L:M] is [2:1] according to the (Fig. (3)) [9]:

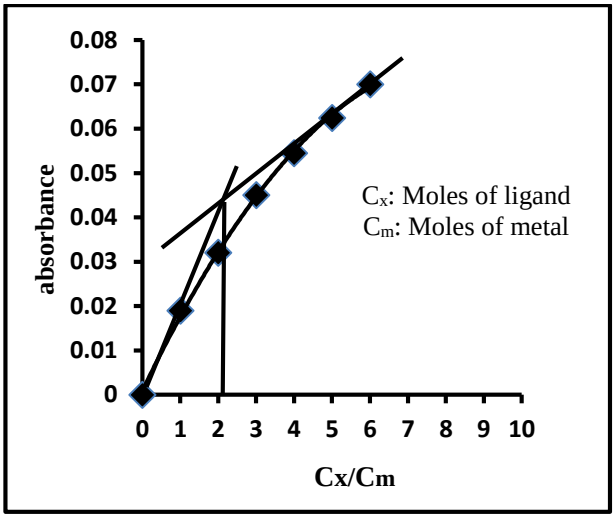

Fig. (3) The mole ratio method.

Atomic Absorption Measurements

A 0.001g of [Bis(1,10)-phenanthroline) nitratolead (II)] nitrate complex was digested in 2 ml of conc. HNO_3. The clear solution was diluted to 10 ml and 1 ml of this solution is again diluted to 10 ml with de ionized water in a volumetric flask. For sample analysis, four standard metal solutions were prepared by appropriate dilution of the metal stock solution with de ionized water. The percentage of pb(II) in the complex is calculated (29.94%) but the found percentage is (30.36%). From this, can be deduced that the proposed molecular weight is (691.62) and the chemical structure for the complex is shows in (Fig. (4)) [8]:

Fig. (4) The chemical structure of prepared complex.

Electronic Spectrum

The electronic spectrum for ligand in ethanol showed three bands at 202 nm (49504cm^{-1}), 228nm (43859cm^{-1}) and 264nm (37878cm^{-1}). They are due to $\pi \rightarrow \pi^*$ (C=C), and $n \rightarrow \pi^*$(C=N) transitions, while the electronic absorption spectrum for Bis [(1,10-phenanthroline)nitratolead(II)] nitrate complex was recorded in ethanol at room temperature. It is helpful in determining the stereochemistry of the complex based on the position and number of transitions peaks. The bands at 236nm (42372cm^{-1}), 261nm (38314cm^{-1}) and 341nm (29325cm^{-1}) are due to $\pi \rightarrow \pi^*$ (C=C), and $n \rightarrow \pi^*$ (C=N) transitions. This shift is due to complexation. The band at 541 nm (18484cm^{-1}) is due to d-d transition [10]. (Figs. (5) and (6)) show the electronic spectrum of ligand and its complex:

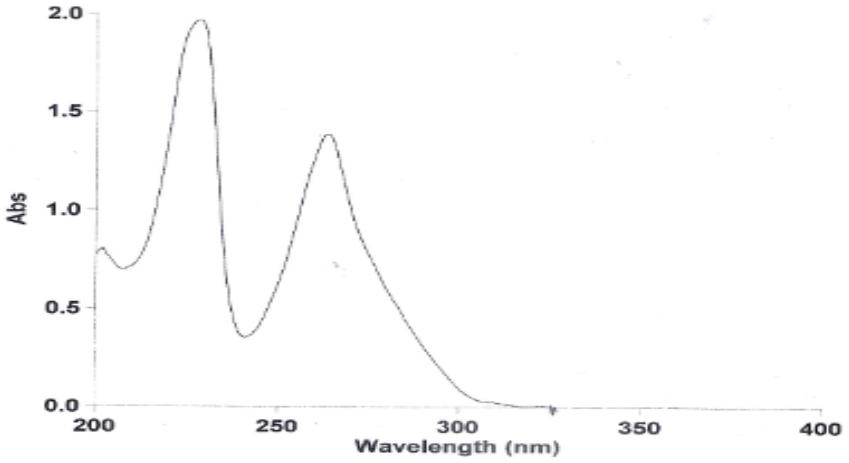

Fig. (5) The electronic spectrum of 1,10-phenanthroline ligand.

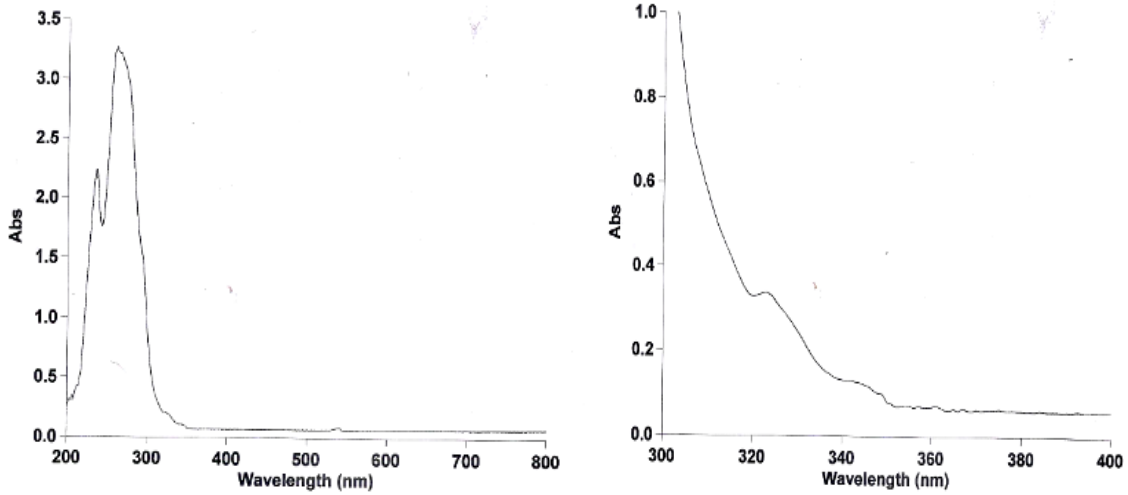

Fig. (6) The electronic spectrum of Bis(1,10-phenanthroline) nitratolead(II)]nitrate complex.

Infrared Spectrum

1,10-phenanthroline ligand contains peaks due to groups which component for 1,10-phenanthroline molecule but the important peak is $\upsilon_{C=N}$ at(1620cm^{-1})region, the region (1421cm^{-1}) which due to $\upsilon_{C=C}$ and (3034cm^{-1}) due to υ_{C-H}, while the complex [Bis(1,10-phenanthroline) nitratolead (II)] nitrate was noticed a change in active peaks [11]. The band $\upsilon_{C=N}$ was shifted to (1624cm^{-1}) and $\upsilon_{C=C}$ shifted to (1384cm^{-1}). These frequencies shifts proved that the metal ions were coordinate with ligand through N atoms. Anew peaks were appeared due to υ_{Pb-O} at (632-557)cm^{-1}, υ_{Pb-N} at(466-408)cm^{-1} and υ_{N-O} at (1512cm^{-1}) [12]. (Figs.(7) and (8)) show the infrared spectrum of 1,10-phenanthroline and its complex:

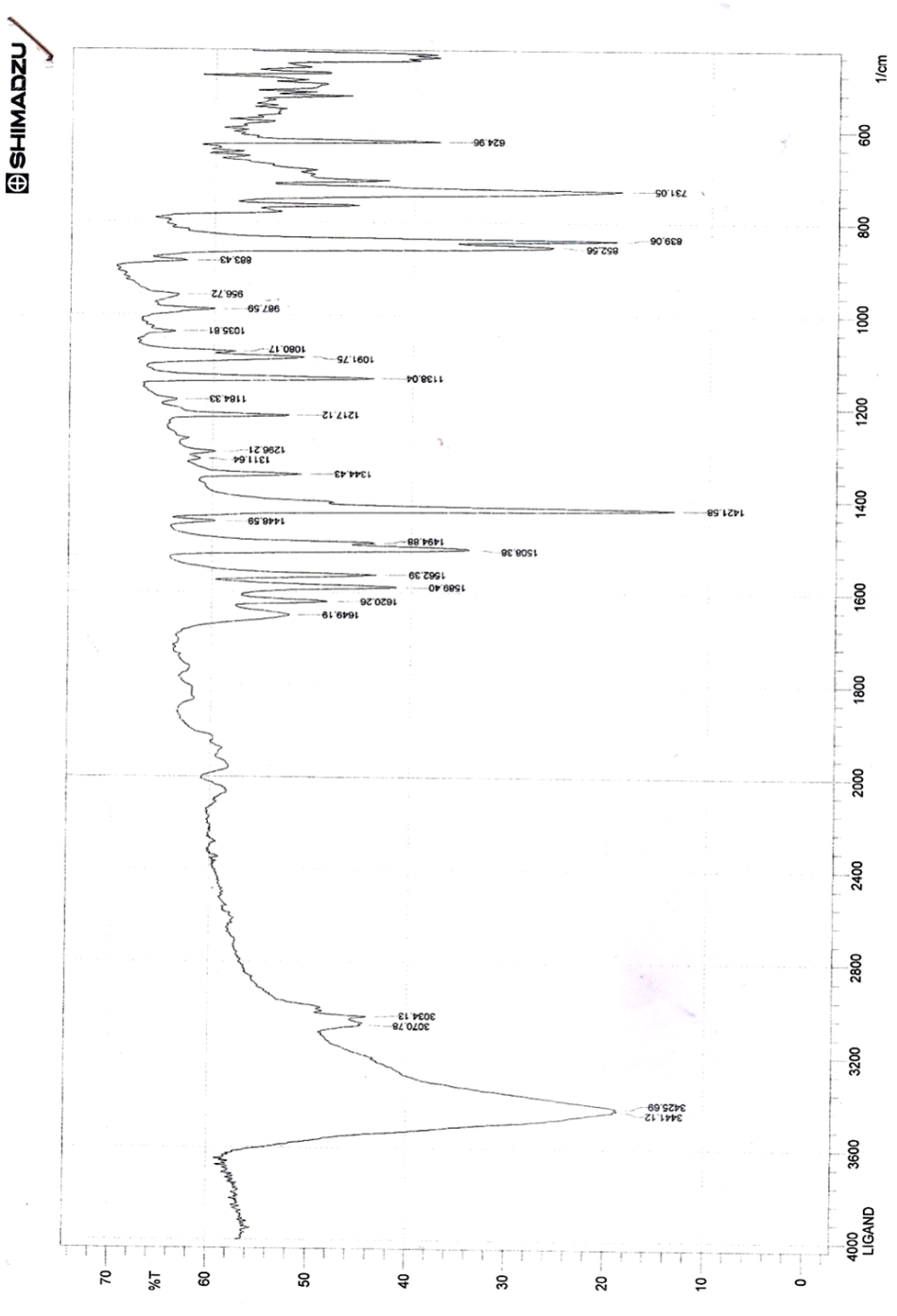

Fig. (7) The IR spectrum of 1,10-phenanthroline ligand.

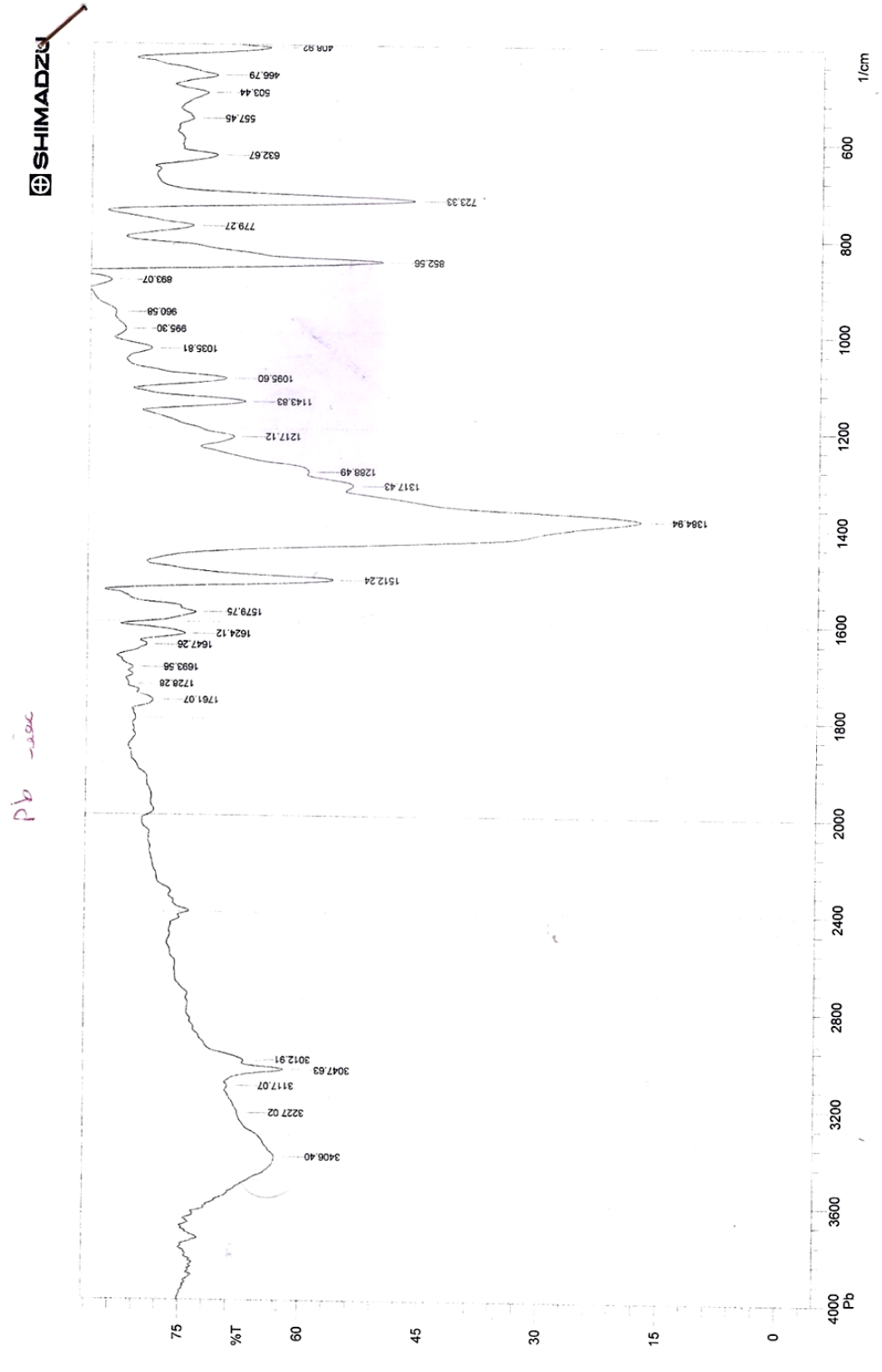

Fig. (8) The IR spectrum of [Bis(1,10-phenanthroline) nitratolead (II)]nitrate complex.

Adsorption Study

-Effect of Temperature

The adsorption study was carried out for [Bis (1,10-phenanthroline) nitratolead (II)] nitrate complex on (activated carbon, zeolite and mixture of them) at different temperatures (25, 30, 35, 40, 45, 50)C^0 using constant concentration of complex solution and the study results show in (Table (2)) and (Fig.(9)):

Table (2)

Adsorption quantities of complex in different temperatures at 60min.

Adsorbents	*C_0 (ppm)*	*Ce (ppm)*	*Temp. (C^0)*	*$Q_e \times 1000$*
Activated Carbon	**10**	**23.1**	**25**	**1.31**
		69.1	**30**	**5.91**
		46.3	**35**	**3.63**
		56.25	**40**	**4.63**
		48	**45**	**3.8**
		40.25	**50**	**3.03**
Zeolite	**10**	**161.95**	**25**	**15.195**
		135.4	**30**	**12.54**
		179.95	**35**	**16.5**
		172.3	**40**	**16.23**
		173.2	**45**	**16.32**
		266.8	**50**	**24**
Mixture of (Activated Carbon & Zeolite)	**10**	**176.45**	**25**	**16.645**
		134.05	**30**	**12.405**
		102	**35**	**9.2**
		144.15	**40**	**13**
		126.7	**45**	**11.67**
		200.45	**50**	**19**

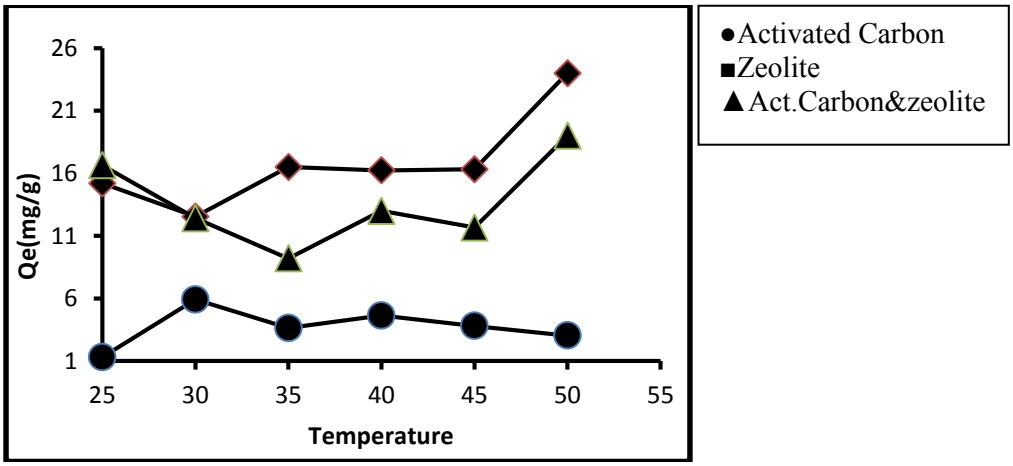

Fig. (9) Temps. Effect on adsorption quantities of complex at 60min.

Was observed from table data that adsorbents activity in the adsorption of complex from aqueous solution as follow [13]:
Zeolite > Activated Carbon & Zeolite > Activated Carbon

-Effect of Contact Times

The adsorption of [Bis(1,10-phenanthroline) nitratolead(II)]nitrate complex on activated carbon, zeolite and mixture of them at different times (30, 60, 90, 120, 150)min using constant concentration of complex solution at $30C^0$. The results show in (Table (3)) and (Fig.(10)):

Table (3)
Adsorption quantities of complex in different times at $30C^0$.

Adsorbents	*C_0 (ppm)*	*C_e (ppm)*	*Time(min)*	*$Q_e \times 1000$*
Activated Carbon	**10**	**28.85**	**30**	**1.885**
		39	**60**	**2.9**
		39.55	**90**	**2.955**
		19.35	**120**	**1**
		21.1	**150**	**1.11**
Zeolite	**10**	**213.2**	**30**	**20.32**
		159.8	**60**	**14.98**
		160.35	**90**	**15.035**
		131.05	**120**	**12.11**
		109	**150**	**10**
Mixture of (Activated Carbon & Zeolite)	**10**	**131.15**	**30**	**12.112**
		192.65	**60**	**18**
		168.9	**90**	**16**
		94.95	**120**	**8.495**
		105.7	**150**	**9.57**

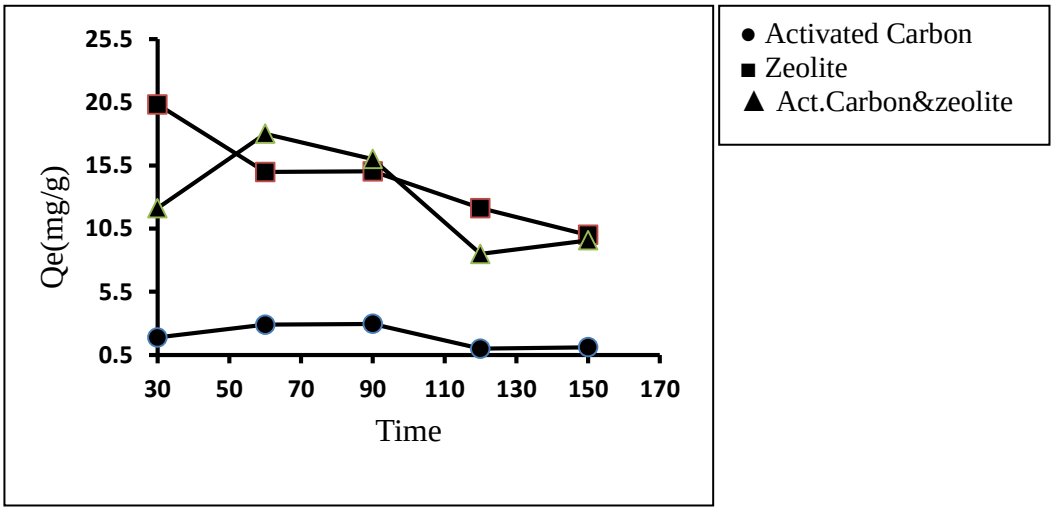

Fig. (10) Times effect on adsorption quantities of complex at $30C^0$.

As the contact time was increased, the amount of adsorption of the complex on all adsorbents also increased. This trend is consistent between (30 -90) minutes contact time when equilibrium was attained. Further increase of contact time beyond 90 minutes generally results in decrease in the adsorption of complex [14].

-Effect of Adsorbents Weights

The adsorption study was carried out for [Bis (1,10-phenanthroline) nitratolead (II)] nitrate complex on activated carbon, zeolite and mixture of them at different of adsorbent weights (0.05, 0.1, 0.15, 0.2, 0.25, 0.3)grams using constant concentration of complex solution at $30C^0$ for 60min and the study results show in (Table (4)) and (Fig.(11)):

Table (4)
Adsorption quantities of complex in different weights of adsorbents at $30C^o$.

Adsorbents	*C_0 (ppm)*	*C_e (ppm)*	*Wt. of adsorb.(gm)*	*$Q_e \times 1000$*
Activated Carbon	**10**	**36.6**	**0.05**	**2.66**
		15.35	**0.1**	**1**
		93.75	**0.15**	**8.375**
		63.7	**0.2**	**5.37**
		62.9	**0.25**	**5.29**
		60.75	**0.3**	**5.075**
Zeolite	**10**	**130**	**0.05**	**12**
		150.85	**0.1**	**14.085**
		150.1	**0.15**	**14.01**
		236.25	**0.2**	**22**
		265.8	**0.25**	**25**
		309.2	**0.3**	**29**
Mixture of (Activated Carbon & Zeolite)	**10**	**95.15**	**0.05**	**8.515**
		113.35	**0.1**	**10.335**
		119.65	**0.15**	**10.965**
		145.2	**0.2**	**13.52**
		163.45	**0.25**	**15.345**
		122.2	**0.3**	**11.22**

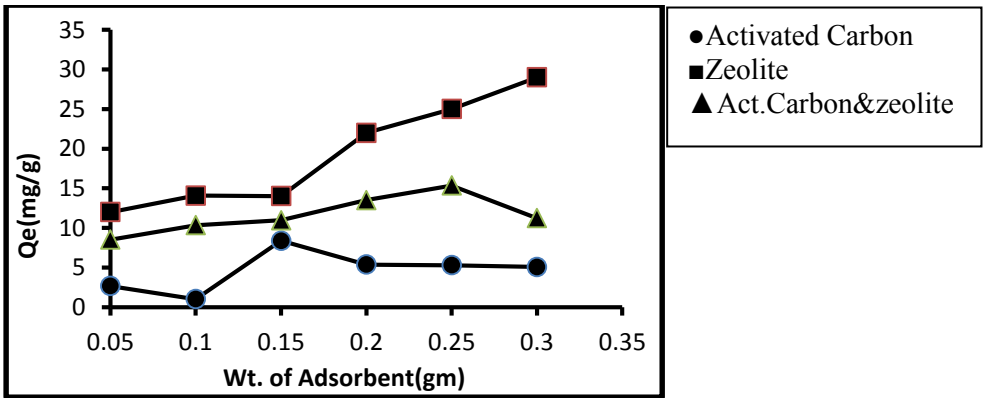

Fig. (11) Wt. of adsorbents change effect on adsorption quantities of complex at $30C^0$.

It was observed that the adsorption quantity of complex on activated carbon decreased when the weight of adsorbent increased that similar observation has been reported by (Sawsan A. M. Mohammed, Ibtihage Faisal and Maha M. Alwan), while the adsorption quantity of zeolite and (mixture of activated carbon and zeolite) increased when the weights of them are increased because zeolite adsorbent is better than activated carbon in the adsorption [15].

-Effect of pH

Adsorption study was carried out for [Bis (1,10-phenanthroline) nitratolead (II)] nitrate complex on activated carbon, zeolite and mixture of them at different pH (2, 5, 7, 9, 11) using constant concentration of complex solution and constant weight of adsorbent 0.1gm at $30C^0$ for 60min and the study results show in (Table (5)) and (Fig. (12)):

Table (5)
Adsorption quantities of complex in different pH at $30C^0$.

Adsorbents	*C_0 (ppm)*	*C_e (ppm)*	*pH*	*$Q_e \times 1000$*
Activated Carbon	**10**	**16.65**	**2**	**0.665**
		27.35	**5**	**1.735**
		54.75	**7**	**4.475**
		73.6	**9**	**6.36**
		59.7	**11**	**4.97**
Zeolite	**10**	**38.45**	**2**	**2.845**
		98.55	**5**	**8**
		72.8	**7**	**6.28**
		167.25	**9**	**15**
		121.75	**11**	**11.175**
Mixture of (Activated Carbon & Zeolite)	**10**	**115.05**	**2**	**10.505**
		208.55	**5**	**20**
		157.15	**7**	**14.715**
		186.55	**9**	**17.655**
		189.85	**11**	**17.985**

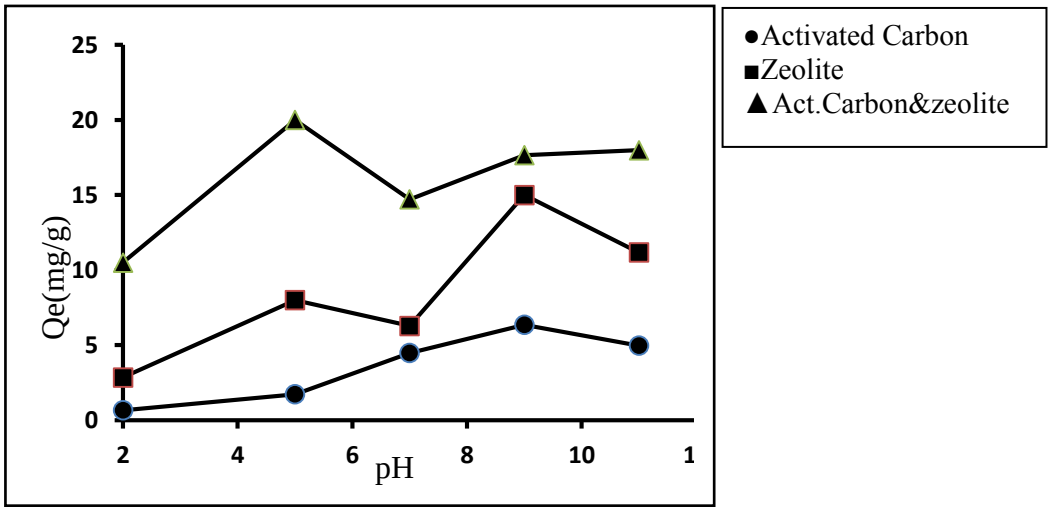

Fig. (12) pH effect on adsorption quantities of complex at $30C^0$.

There is a significant difference in adsorption due to the influence of pH for activated carbon, zeolite and the mixture of them. The effective pH range for activated carbon was 5 to 11, for zeolite it was 5 to 11 and for the mixture it was above 2. In the three cases there are a convergence from side of increasing in the adsorption quantities with the increasing of pH values [7].

Conclusions

1- The complex [Bis (1,10-phenanthroline) nitratolead (II)] nitrate was prepared by using the analytical instruments (IR, UV) spectroscopy, conductivity meter and atomic absorption to analyze the complex and use it in the adsorption.

2- This complex was used in the adsorption on activated carbon, zeolite and mixture of them. Were concluded from this recent study that's the adsorption increased with increasing of adsorbents amount.

3- generally these results show that natural zeolite can be used effectively for the removal of metal cations from wastewater. This naturally occurring material provides a substitute for the use of activated carbon as adsorbent due to its availability and its low cost.

References

[1] Halcrow E. and Kermack W. O., "43. Attempts to find new antimalarials. Part XXIV. Derivatives of o-phenanthroline (7: 8: 3′: 2′-pyridoquinoline)". J. Chem. Soc. pp. 155–157, 1941.

[2] Reiher M., Brehm G., and Schneider S., "Assignment of Vibrational Spectra of 1,10-Phenanthroline by Comparison with Frequencies and Raman Intensities from Density Functional Calculations" J. Phys. Chem. (108), pp. 734-742, 2004.

[3] Xiang Li C. , Lin Zha X., Bo Liu C., Ying Li X. and Bo Che G., "Bis (imidazo [4,5-f][1,10] phenanthroline) dinitratolead (II)" Acta Crystallogr Sect E Struct Rep Online.; 65 (Pt 1): m54, 2009.

[4] Shahverdizadeh G. H. , Weng Ng S., Tiekink E. R. T. and Mirtamizdoustd B., "*catena*-Poly [[(1,10-phenanthroline-κ^2 *N*,*N*′) lead(II)]-di-μ-nitrato-κ^3 *O*,*O*′:*O*″;κ3 *O*:*O*′,*O*″- [(1,10-phenanthroline-κ^2 *N*,*N*′) lead(II)]-bis(μ-2,2,2-trichloroacetato-κ^2 *O*:*O*′)] Acta Crystallogr Sect E Struct Rep Online.; 68(Pt 3): m237–m238, 2012.

[5] Peric J., Trgo M. and Medvidovic N. V., "Removal of zinc, copper and lead by natural zeolite - a comparison of adsorption isotherms" Water Research 38, pp. 1893–1899, 2004.

[6] Sekar M., Sakthi V. and Rengaraj S., "Kinetics and equilibrium adsorption study of lead (II) onto activated carbon prepared from coconut shell" Journal of Colloid and Interface Science 279 , pp. 307–313, 2004.

[7] Payne K. B. and Abdel-Fattah T. M., "Adsorption of Divalent Lead Ions by Zeolites and Activated Carbon: Effects of pH, Temperature, and Ionic Strength" Journal of Environmental Science and Health, Vol. A39, No. 9, pp. 2275–2291, 2004.

[8] Woubie M. W., "Synthesis and characterization of Ni(II) and Zn(II) Complexes of Multidentate ligand Derived from 1,10-phenanthroline-5,6-dione and O-phenanthroline" Department of Chemistry, Addis Ababa University, CHEM. 774, 2010.

[9] Wear J. O., "Mathematics of The Variation and Mole Ratio Methods of Complex Determination" Arkansas Academy of Science Proceedings, Vol. 22, 1968.

[10] Rasheed R. T. and Eessa H. A., "Synthesis of Metal Complexes Derived from Salicylidene p-Aminoacetophenone" Eng. & Tech. Journal, Vol. 30, No. 14, 2012.

[11] Silverstein R. M. and Webster F. X., "Spectrometric Identification of Organic Compounds" 6th edition, John Wiley & Sons, 1998.

[12] El-Ajaily M. M. and El-Saied F. M., "Synthesis and Characterization of Urea Schiff Base Chelates of Cr(III), Cr(VI), TiO(IV) and Pb(II)" Asian Journal of Chemistry, Vol. 19, No. 6, pp. 4433-4437, 2007.

[13] Erdem E., Karapinar N. and Donat R., "The Removal of Heavy Metal Cations by Natural Zeolites" Journal of Colloid and Interface Science 280, pp. 309–314, 2004.

[14] Elaigwu S. E., Usman L. A., Awolola G. V., Adebayo G. B. and Ajayi R. M. K., "Adsorption of Pb (II) from Aqueous Solution by Activated Carbon Prepared from Cow Dung" Advances in Natural and Applied Sciences, 3(3), pp. 442- 446, 2009.

[15] Mohammed S. A. M., Faisal I. and Alwan M. M., "Oily Wastewater Treatment Using Expanded Beds of Activated Carbon and Zeolite" Iraqi Journal of Chemical and Petroleum Engineering, Vol.12, No.1, 2011.

الخلاصة

تم في هذا البحث تحضير معقد [Bis(1,10-phenanthroline)nitratolead(II)]nitrate ودراسة امتزاز المعقد على سطوح (الكاربون النشط، الزيولايت ومزيج من السطحين) بأوزان متساوية وتحت ظروف مختلفة مثل التغير في: درجة الحرارة، وقت ارتباط السطح بالمحلول، pH المحلول والتغير في اوزان السطوح. بالنسبة للكاربون النشط فأن كمية الامتزاز ازدادت عند درجة حرارة تتراوح بين C^0 (٣٠-٥٠) وبزمن min(٦٠-٩٠) والوزن المثالي للامتزاز (٠,١٥g) عند pH(٩)، اما الزيولايت فأن كمية الامتزاز ازدادت عند درجة حرارة وصلت الى (C^0 ٥٠) وبزمن اقل من (90 min) وبوزن (0.3 g) و pH (٩)، واخيرا عندما تم مزج السطحين مع بعضهما وبأوزان متساوية فأن كمية الامتزاز ازدادت عند درجة حرارة وصلت الى (C^0 50)، بزمن يتراوح بين (60-90 min) وبوزن (0.25 g) وعند pH(5-11).